4TH EDITION

PVC DEGRADATION AND STABILIZATION

GEORGE WYPYCH

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PVC
Degradation & Stabilization
3nd Edition

George Wypych

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Chemical Structure of PVC

From Staudinger's time it has been known that PVC has a lower thermal stability than comparable low-molecular weight compound such as 1,3,5-trichlorohexane.[1] Since then it has been established in many publications[2-5] that PVC undergoes chemical change if the temperature exceeds 373K, which is at least 100K less than should be expected based on an analogy to low-molecular weight substances of similar structure such as 1,4,7-trichloroheptane, 2,4-dichloropentadecane, and so on. It was, therefore, quite natural that, from the beginning of studies on PVC thermal stability, irregularities in the polymer chain have been taken into consideration.

Because of the complicated nature of the polymerization reaction mechanisms, numerous structural defects might be expected (see more on this subject in the next chapter). The evaluation of potential dangers of degradation must include polymerization technology, PVC morphological structure, thermal treatment during production and processing, and composition of various additives used in the PVC processing. We will review these subjects in several chapters of this book. This chapter contains information on the chemical structure of polyvinylchloride.

1.1 REPEAT STRUCTURES AND THEIR BASIC ORGANIC CHEMISTRY

Poly(vinyl chloride) contains three basic bonds: C–C, C–H and C–Cl. Table 1.1 shows the average bonds' properties.

Table 1.1. Average properties of basic PVC bonds.

Bond	Bond length, pm	Atomic radius, pm	Bond dipole moment, Debye
C–C	154	C=77	0
C–H	109	H=37	0.30
C–Cl	177	Cl=100	1.56

The C–C bond length may vary in a broad range; for example, the values of 134 pm and 120 pm have been given for the double bond in alkenes and the triple bond in acetylene compounds, respectively. Also, the presence of double bonds in the close neighborhood of a single bond between two carbon atoms will affect its length (e.g., a single bond in 1,3-butadiene has a length of 148 pm). Single bond length varies depending on its position in α-alkane chain from 152.34 to 152.46 pm (picometers=10^{-12} m).[1a] For all-trans n-alkanes, the proton affinities (ΔH^{298}) vary from 142 kcal mol^{-1} (for ethane) to over 166 kcal mol^{-1} and increase monotonically from the end of the alkane chain to the center.[1a]

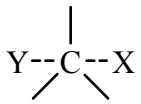
Similar bond length variations are noted in the case of the C–Cl bond, which may vary in the range of 164-178 pm. The decrease in bond length has been interpreted in terms of about 10-20% double bond character of the C–Cl bond, caused by conjugation of an unshared pair of electrons of the chlorine atom with the double bond or aromatic nucleus. Also, the s-character of the carbon atom results in a bond length change with the highest value for $C(sp^3)$–Cl and the lowest for C(sp)–Cl. Similar changes affect C–C and C–H bond lengths, but they are more pronounced in the case of the C–Cl bond than the C–C bond and the C–H bond. The electronegativity of atoms bound to the carbon atom is responsible for the further changes in the C–Cl bond length. The differences are not large but the effect can influence ground-state stabilization and therefore modify the rates of reaction and equilibrium constants.

Covalent radii, by their nature, are expected to be as sensitive as bond length to hybridization differences at the carbon atoms, electron-delocalization, electronegativity differences, ionic character, and steric effects. There are substantial differences in the character of the three bonds discussed. While the C–C bond is non-polar and the C–H bond only slightly polar, the C–Cl bond is very close to an ionic bond in character. This influences the reactivity of these bonds and the mechanisms of reactions occurring when they are energetically unstable.

It is interesting to note that the dipole moment of vinyl chloride is 1.45 Debye (very close to the average dipole moment of C–Cl bond given in Table 1.1). The polarity of a polyatomic molecule can be expressed in terms of its dipole moment – a vector sum of all bond dipoles of the molecule. This vector sum accounts for the direction of the bond dipole and the angles between the bonds of the molecules in order to obtain the resultant dipole vector of the molecule. It is therefore evident that chemical properties of polyvinyl-chloride are dominated by properties of the C–Cl bond.

This is further supported by differences in electronegativity of atoms forming PVC (C – 2.6, H – 2.2, Cl – 3.2). The greater the electronegativity difference between two atoms, the more ionic the bond. In the case of polyvinylchloride, C–Cl has a strong ionic character.

Table 1.2 shows the bonds' dissociation energies. The same type of bond is broken in each case, with bond dissociation energy varying considerably. For C–H bonds the energy gap equals 79 kJ/mol, and for C–Cl bonds, 66 kJ/mol. In both cases the electron-with-drawing groups contribute to bond energy decrease as it occurs according to the order of the carbon atom. Considerably low dissociation energy of the C–C bond (347 kJ/mol) may suggest that it could be vulnerable to chemical reactions, which would be true if that factor alone could contribute to the reaction rate. Since carbon has a relatively small nucleus with a maximum covalence of four and it is able to expand its octet by the use of d-orbitals only with the expenditure of much energy, any transition state involving a fifth bond to the carbon atom has to accommodate the five groups around carbon in excessive electron-density. The geometry of the structural arrangement is thought to be as shown:



A consequence of the crowded structure of the carbon atom in the transition state is that bulky groups introduced at the reaction center are generally associated with a decreased reaction rate.

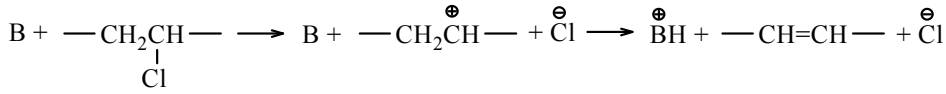
Table 1.2. Bond dissociation energy.

Bond	ΔH, kJ/mol
CH_3–H	435
$(CH_3)_2$CH–H	395
CH_2=$CHCH_2$–H	356
C_6H_5–CH_2–H	356
CH_3–Cl	351
$(CH_3)_3$C–Cl	331
$C_6H_5CH_2$–Cl	285

Comparing the C–H and C–Cl bonds, we may expect that the C–Cl bond should dissociate more easily for two reasons: first, because the energy barrier is lower, and second, because the electric charge dislocation facilitates the chemical reaction.

To better understand the subject under discussion and the complexities of the bonds' nature, one should review typical mechanisms of reactions.

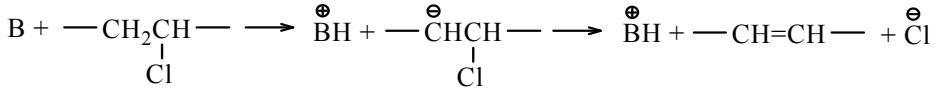
Elimination of the E1 type proceeds through the intermediary of the carbonium ion. The sequence of reactions could be written for the VC monomer in the following form:



Several factors are known to favor this reaction mechanism. One is the presence of polar solvents in the reacting mixture. Reactions in solution might follow different routes without polar solvents, as there is a substantial change in energy during reaction and because of participation of solvation energy. Sometimes these changes in energy are more important for the reaction course than is the strength of forming and breaking bonds. If we also consider collision mechanics in the solution, the probability of such collisions, and the number of encounters, we may conclude that the presence of solvent might play the most important role for the reaction mechanism and for the reaction rates.[6] On the other hand, the solvent might also contribute to the energy transfer from the molecular fragment in vibrational mode which otherwise would lead to a transitional state, and therefore, it can act in collisional deactivations.

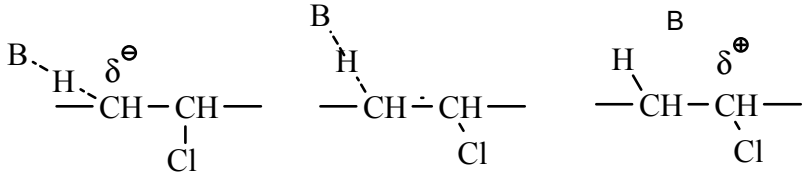
The elimination reaction of the E1 type will also be favored by a good leaving group. Chlorine might be considered as such a group. Finally, the presence of any group at the position which stabilizes the carbonium ion would contribute to the E1 mechanism's prevalence. This reaction mechanism is especially characteristic for the tertiary and secondary alkyl halides.

The elimination reaction according to the E1cB mechanism includes carboanion as the intermediate:



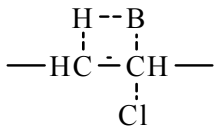
The presence of an acidic β–proton is thought to increase the rate of carboanion formation.

A poor leaving group should slow down E2 elimination and favor carboanion formation. Among halogens, fluorine forms the poorest leaving group, and chlorine is the second in sequence. The E2 mechanism depends on an energy imbalance introduced in the transitional states described below:



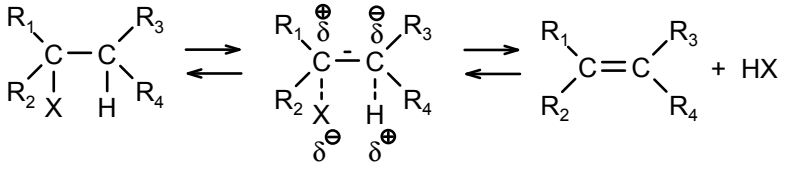
The character of the transitional state determines the degree of C–H and C–Cl bond breaking. In the course of the elimination reaction, any group formed or any change in reaction conditions which might affect the charge distribution or activation process favors the particular direction of the elimination process. In the case of the PVC monomeric fragment, the leaving group, that is, HCl, will stabilize the carboanion structure in relation to the carbonium ion and thus increase C–H bond breaking. For the carboanion transition state the β-substituents of the electron-withdrawing character (e.g, double bonds) should increase the carboanion character and favor C–H bond breaking. Reacting base B might also contribute to the reaction mechanism due to its nucleophilicity.

The E2C transition states have the following structure:



E2C elimination is favored by dipolar aprotic solvents such as DMF and any good leaving group (e.g., Cl). Also, substrates, having tertiary carbon atoms, will undergo changes according to this mechanism more easily.

Another mechanism, known in the literature under the name of four-center HX elimination, might help explaining the course of the PVC degradation process. This mechanism was suggested on the basis of studies of unimolecular elimination of HX from alkyl halides. The possibility of partial charge separation was proven quite early.[7] Further studies of the reaction and its activation energy parameter for many alkyl monohalides confirmed the polar nature of reaction and the existence of surface catalysis.[8] The essence of the above mechanism can be explained by the following equation:



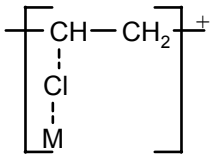
It has been established that methyl and other n-alkyl groups bound to the α-positioned carbon atom participate in the stabilizing effect. The chlorine atom affects the formation of the positive charge on the carbon atom to which it is bound, but it does not contribute to the formation of a negative charge on the neighboring β-carbon. The effect just described contributes to C–X bond energy, which, together with H–X bond dissociation energy, determines the rate of initiation. The presence of HX can promote autocatalytic reactions. Overall, one might expect a dehydrochlorination reaction of the first order to take place.

Molecular elimination of HX is usually preferred in the case of primary and secondary carbon atoms, while the radical route might prove to be essential when halides are bound to tertiary carbon atoms. The activation energy in the four-center elimination process is drastically decreased when methyl, vinyl, aromatic groups or oxygen are bound to a carbon atom which forms a C–X bond at the same time. If one of these groups is bound to a carbon atom forming a C–H bond, the effect is negligible or not as strongly pronounced as in the other case. This might suggest that if one considers the regular distribution of the C–X bonds at each second carbon atom, which is generally the case in PVC, one may expect reaction to proceed along the chain until the first irregularity appears, which might be why reaction is terminated for that center.

Having completed this brief listing of the major mechanisms believed to be essential for explaining the nature of the HX elimination process, we still need to describe the reaction which involves the substitution of chlorine by other groups in the course of the same reaction. Two well-known mechanisms of substitution have been used in organic chemistry for years: the S_N1 and S_N2 types. The mechanism S_N2 resembles some features of elimination mechanism, E2, and mechanism S_N1 competes with elimination of the E1 type because they share carbocation intermediate. For our studies, it is essential to notice the differences between both mechanisms in respect to reactions which may occur if segments of the PVC chain are thermodynamically unstable and therefore able to react. As we concluded above, the carbon atom, because of its four-valent character and its need to form a crowded transition state, including accommodation of five groups, is not the easiest one to undergo substitution reaction. Referring that to the mechanism of S_N2 type, which

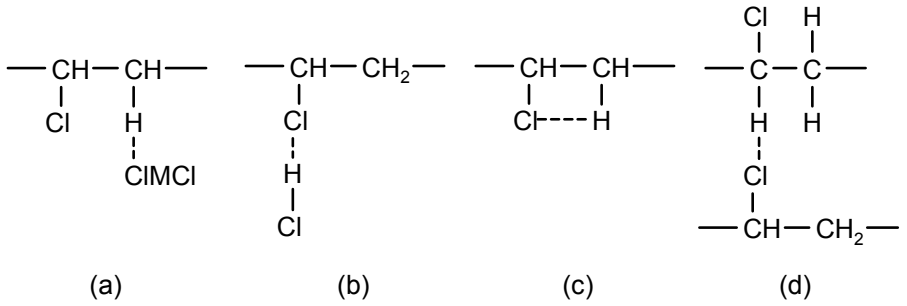
includes such a transition state, one might expect that the substitution of chlorine by any other group according to the S_N2 mechanism would be more likely to occur in the case of secondary than tertiary carbon atoms in α- and β-positions to the reaction center. Thus, all the branches available at the reaction site will form unfavorable geometric hindering effects for the reaction to be performed. This is in complete contradiction to the conditions which might favor reaction of the S_N1 type, which is more likely to occur when a C–Cl bond is formed with a tertiary carbon atom. On the other hand, electron-attracting groups (e.g., double bonds) will promote the S_N2 mechanism and retard S_N1. Therefore, if substitution of unstable chlorine bound to a tertiary carbon atom takes place, it is likely done through a mechanism of the S_N1 type at the beginning of the degradation process before unsaturated fragments are formed.

The S_N1 mechanism includes the formation of a carbonium ion in the first step of the reaction. Therefore, it is favored by a good-leaving group, polar solvents and α-substituents, which stabilize the carbonium ion. The stabilizing α-substituents prolong the accessibility of ions for reaction. One peculiarity in the S_N1 mechanism is potentially useful for explaining the PVC degradation mechanism. Catalysis of PVC dehydrochlorination by metal salts normally appears to be S_N1-like, with a transition state as follows:



The possibility of the catalytic influence of metal salts permits substitution of chlorine at a more advanced stage, e.g., when a C–Cl bond under consideration is already in the neighborhood of a double bond or bonds formed in the former acts. The last remark on the catalytic effect of the metal salts and the earlier one on the catalytic effect of HCl brings us closer to the final topic of this section: the possibility of inter- and intra-molecular hydrogen bonding and its eventual implications.[9]

Formation of the following hydrogen bonds is theoretically possible:



One should take into consideration that in the majority of cases chlorine is the most active halogen in hydrogen bond formation. Usually the energies of hydrogen bonds with

chlorine are in the range of 12 to 42 kJ/mol, which is designated as normal, and some of these bonds have energy above 42 kJ/mol, which is a strong hydrogen bond.

Taking into consideration structure (d), which suggests the formation of an intermolecular hydrogen bond between two chains, the C–Cl bond has a pronounced electron-withdrawing effect upon other bonds associated with the same carbon atom; therefore, the hydrogen atom may become sufficiently acidic so as to act as an electron-acceptor atom in a hydrogen bond. Considering the structure (c), it must be kept in mind that the most stable forms of hydrogen bond occur when the proton-donor and proton-acceptor atoms are colinear. "Bent" hydrogen bonds can occur, but they are weak. Also, the steric effect arising from constraints such as double bonds within the molecule might prevent hydrogen from approaching a chlorine atom. Conversely, the hydrogen group linked to the sequence of conjugated double bonds is a much stronger proton donor.

Reconsidering the mechanism of the four-center HX elimination process from the point of view of the hydrogen bonds available, we see that an intra-molecular hydrogen bond can secure the negative charge on the β-carbon atom and therefore promote the reaction to follow that mechanism.

In respect of structures (a) and (b), one might say that similar bonds have been observed in some compounds, and as catalytic effects are observed in heterophasial systems which are, respectively, liquid-solid and liquid-gas, it is possible that they might occur due to the former hydrogen bond formation which weakens the initial bonds and permits the split-off of hydrogen or chlorine, respectively.

This brief survey of reaction mechanisms is brought for the further discussion of PVC decomposition. The principles of reactions discussed here have been formed on the basis of simple compounds. In fact, the scope of PVC decomposition also concerns participation of small molecules (e.g., HCl, stabilizers, etc.). In many other cases, the reactions occur due to a single collision that does not involve the whole chain but only its small fragment, which is in proper energetic condition and might behave like a moiety of low molecular weight, especially if the collision occurs with a small molecule. In the following chapters, many different aspects of organic synthesis are considered and some of them can be described by these fundamental principles.

1.1.1 BRONSTED ACID SOURCE WITH CONTROLLABLE EMISSION

The previous section indicates that dehydrochlorination can be considered to be a reaction which dominates chemical changes of PVC. In a recent publication,[10] PVC was considered and used as a source of Bronsted acid.

In 1923, Danish physical chemist J. N. Bronsted and T. M. Lowry of England put forward the acid-base concept which is one of the major principles of today's chemistry. According to their concept, acids donate and bases accept protons. Both reactions of elimination presented in the previous section show transfer of protons from PVC to a base with formation of an ionic pair capable of further reactions.

PVC was called a Bronsted acid source with controllable emission[10] because it was possible to control the rate of HCl formation by PVC photosensitization with hydroquinone. In this experiment, photosensitized PVC was combined with emeraldine base of polyaniline and subjected to UV radiation. Elimination of HCl leads to formation of con-

jugated double bonds which ultimately leads to polyacetylene – a conductive polymer. On the other hand, a volatile product of reaction – HCl – is used for *in situ* doping of emeraldine base of polyaniline to make it conductive.

In a similar experiment,[11] PVC was used for lithographic purposes. HCl formed in a similar process was used to change the color of methyl violet.

These two of many examples show unusual applications of major reaction in polyvinylchloride degradation process which is a subject of many studies and practical applications of stabilization.

The Bronsted acid principle is also associated with the catalysis of PVC dehydrochlorination. Owen pointed out that $H^{+}ZnCl_3^{-}$ is the most effective catalytic moiety in PVC dehydrochlorination reaction.[12] Later Gerard[13] confirmed, by electronic and resonance Raman studies, that polyene-metal salt complexes are formed, even when zinc chloride is replaced by stannous chloride. Later, Tran *et al.* included this mechanism in their polaron mechanism of thermal stabilization.[14]

In summary, the concept of Bronsted acid-base is one of the fundamental principles governing chemistry of PVC degradation and stabilization.

1.2 MOLECULAR WEIGHT AND ITS DISTRIBUTION

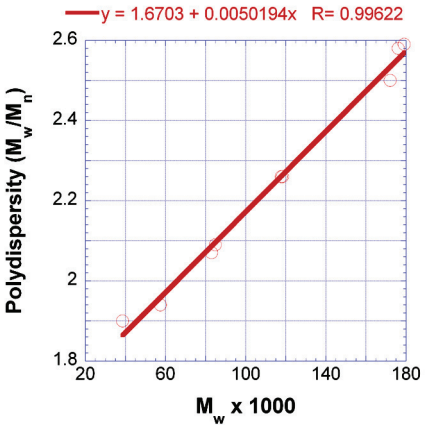


Figure 1.1. Polydispersity of suspension PVC vs. its weight average molecular weight. [Data from Pepperl, G., *J. Vinyl Additive Technol.*, **6**, 2, 88-92, 2000.]

Polyvinylchloride is synthesized by several different methods of polymerization including suspension, mass, and emulsion polymerization (details of polymerization reaction are included in Chapter 2). In the course of synthesis, a mixture of polymer chains is produced having a broad distribution of molecular weights. Molecular weight and its distribution are related as Figure 1.1 shows. Polydispersity of PVC increases with increase in its molecular weight.

Molecular weight is one of the most important properties of polyvinylchloride. There are many examples given in this book which show that molecular weight determines almost all processing and application characteristics. Currently produced polymers have molecular weight tailored to the processing methods and they are optimized to have optimal thermal stability and other properties important for processing and application. Table 1.3 shows molecular weights and polydispersity of commercial polymers.[15,16]

Table 1.3. Typical molecular weight and polydispersity range.[15,16]

Polymerization method	M_n	M_w	M_w/M_n
Suspension	20,32-69,141	38,611-179,123	1.90-2.59
Emulsion	27,173-49,540	61,650-131,191	2.14-2.65
Mass	26,351-37,772	52,683-77,829	2.00-2.06

1.2.1 KUHN-MARK-HOUWINK-SAKURADA

The intrinsic viscosity can be related to a molecular weight with a power law expression known as the Kuhn-Mark-Houwink-Sakurada, KMHS, equation:

$$[\eta] = KM_v^a \qquad [1.1]$$

where:

$[\eta]$ intrinsic viscosity
K, a constants
M_v molecular weight calculated based on viscosity measurements.

Molecular weight obtained from this equation is not an absolute measure because it depends on solvent and molecular weight distribution.

1.2.2 FIKENTSCHER K NUMBER

Fikentscher derived the K number in 1932 from measurements of the relative viscosity of dilute polymer solutions. The k value is calculated from the following equation:

$$\log\frac{\eta_c}{\eta_0} = \left(\frac{75k^2}{1 + 1.5kc} + k\right)c \qquad [1.2]$$

where:

η_c viscosity of solution
η_0 viscosity of solvent
k constant
c concentration in g/100 mol.

Fikentscher K number is given by equation:

$$K = 1000k \qquad [1.3]$$

The Fikentscher K number is very commonly used in polyvinylchloride. Commercial polymers have K number usually in the range of 50 to 90. Fikentscher K number should not be confused with the K constant of the Kuhn-Mark-Houwink-Sakurada equation.

1.2.3 CHAIN LENGTH

The Flory-Fox equation gives dependence between chain length and glass transition temperature. The equation was modified O'Driscoll *et al.*[17] to fit experimental data for major polymers with a fitting coefficient (2/3). The equation takes the following form:

$$T_{g,n} = T_{g,\infty} - \frac{K}{X_n^{2/3}} \qquad [1.4]$$

where:

$T_{g,n}$ glass transition temperature
$T_{g,\infty}$ asymptotic value of glass transition temperature
K polymer-specific constant
X_n the number-average chain length

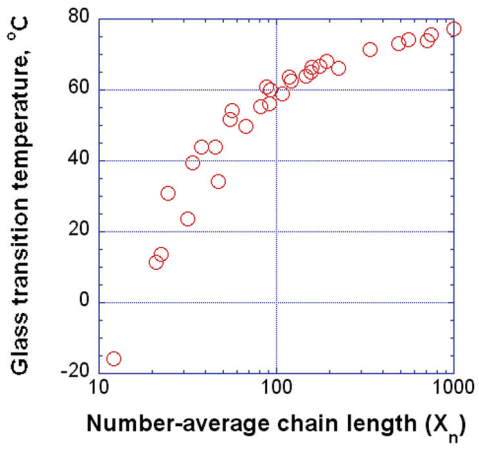


Figure 1.2. Dependence of glass transition temperature of PVC on its number-average chain length. [Data from O'Driscoll, K.; Sanayei, R. A., *Macromolecules*, **24**, 4479-4480, 1991.]

Figure 1.2 shows experimental data for polyvinylchloride.[17] In the absence of a detailed, theoretical model for T_g the modified Flory-Fox equation can be regarded as an empirical expression of the glass transition dependence on chain-length of polymer. An inverse 2/3 dependence on chain length has also been experimentally observed and modeled for both the polymer surface tension and the interfacial tension of immiscible polymers. New research may help in clarification and better understanding of this equation.

1.3 PREDICTION OF FORMATION OF IRREGULAR SEGMENTS

1.3.1 *AB INITIO*

Ab initio calculations were used to predict formation of irregular segments during PVC synthesis. Table 1.4 gives predicted concentrations of various irregular segments.

Table 1.4. Results of *ab initio* calculation. [Data from Van Cauter, K.; Van Den Bossche, B. J.; Van Speybroeck, V.; Waroquier, M., *Macromolecules*, **40**, 4, 1321-1331, 2007.]

Irregular segment	Concentration in number of groups per 1000 VC mers
chloromethyl branch (tertiary H)	4.3
2,4-dichloro-n-butyl branch	0.14
1-chloro-2-alkene end group	1.4
1,2-dichloroalkane end group	1.4
1,2-dichloroethyl branch	0.020

Table 1.4. Results of *ab initio* calculation. [Data from Van Cauter, K.; Van Den Bossche, B. J.; Van Speybroeck, V.; Waroquier, M., *Macromolecules*, **40**, 4, 1321-1331, 2007.]

Irregular segment	Concentration in number of groups per 1000 VC mers
internal allylic group	6.4×10^{-3}
long chain branch (tertiary Cl)	5.9×10^{-4}
long chain branch (tertiary H)	7.3×10^{-4}
1,3-dichloroalkane end group	9.1×10^{-4}
1,3-bis(2-chloroethyl) branch	6.9×10^{-5}
chloromethyl branch (tertiary Cl)	3.3×10^{-10}
pentyl branch	3.8×10^{-9}

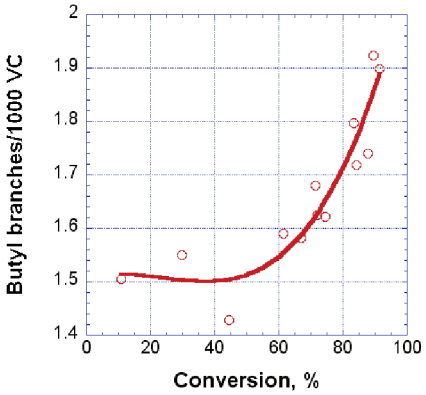


Figure 1.3. Number of butyl branches per 1000 VC vs. monomer conversion as predicted by ab initio calculations. [Data from Purmova, J.; Pauwels, K. F. D.; Van Zoelen, W.; Vorenkamp, E. J.; Schouten, A. J.; Coote, M. L., *Macromolecules*, **38**, 15, 6352-6366, 2005.]

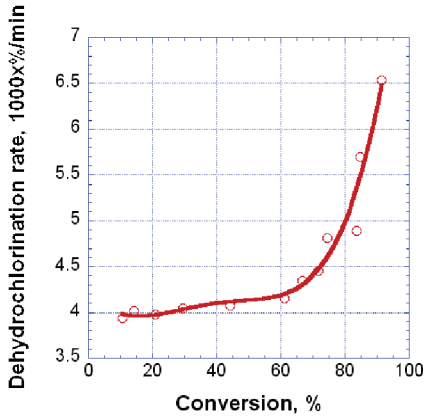


Figure 1.4. Dehydrochlorination rate vs. monomer conversion as predicted by ab initio calculations. [Data from Purmova, J.; Pauwels, K. F. D.; Van Zoelen, W.; Vorenkamp, E. J.; Schouten, A. J.; Coote, M. L., *Macromolecules*, **38**, 15, 6352-6366, 2005.]

The following sections discuss the available literature and experimental data on the formation of these groups. The experimental data can be compared with the predicted data given in Table 1.4. Such comparison will generally show that the *ab initio* method is an excellent tool for predicting outcomes of PVC synthesis.[18]

Figures 1.3 and 1.4 show prediction of formation of butyl branches vs. conversion and the effect of monomer conversion on dehydrochlorination characteristics of synthesized PVC.[19] Butyl branch concentration vs. conversion is just one example of numerous data generated, which all indicate that high conversions lead to increased concentration of irregular segments. Figure 1.4 further explains that formation of these irregular moieties is a principle reason for polymer dehydrochlorination characteristics.[19]

1.3.2 MONTE CARLO

Monte Carlo simulation was also used to predict the frequency of defect formation. Table 1.5 shows the results.

Table 1.5. Monte Carlo simulation of defect formation. [Data from Guyot, A., *Macromolecules*, **19**, 4, 1090-1105, 1986.]

Irregular segment	Experimental value	Simulation
	Number of defects per 1000 VC	
monochlorinated chain end	2.7	1.1
dichlorinated chain end	3.5	1.22
unsaturated chain end	0.75	0.99
internal unsaturation	0.1-0.45	0.23
chloromethyl branch	3.8	4.0
short branch (from back-biting)	0.8	0.79
long branch	0.1	0.09
tertiary chlorine	0.9	0.88

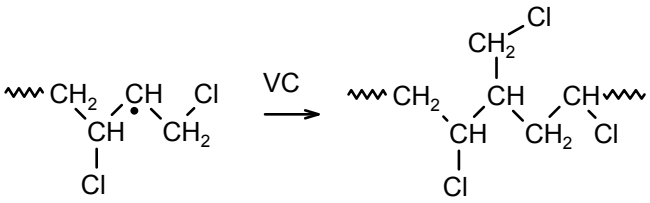
Monte Carlo simulation data are in good agreement with obtained experimental values. It is difficult to compare *ab initio* and Monte Carlo simulation data because selected irregular segments are different but if they were the same there would have been a good correlation between data coming from different methods of simulation.

1.4 IRREGULAR SEGMENTS

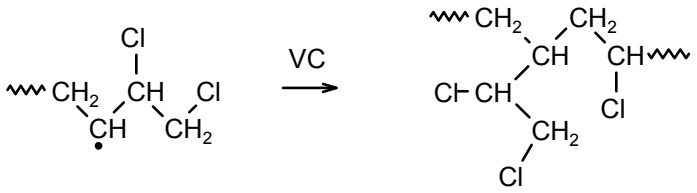
1.4.1 BRANCHES

Poly(vinyl chloride) has a linear structure, but there are some branches of various lengths formed in the polymerization process. The following chemical mechanisms are involved in creation of these branches:

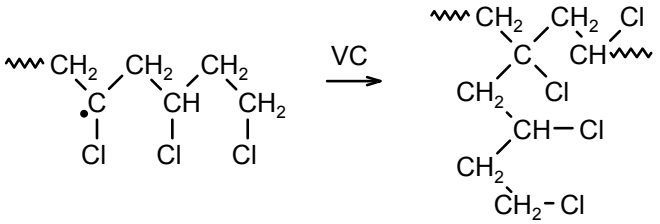
methyl



ethyl



butyl



The long branches are formed according to the same mechanism but by propagation from a different (more distant from the end of chain) radical location. In literature, the short branch term includes methyl, ethyl, and butyl, and long branches have up to 100 mer units.[21] The length of a branch thus depends on the location of a radical. Methyl branches can be formed *via* a possible 1,2-intra- or intermolecular hydrogen abstraction reaction. Methyl branches containing a tertiary Cl may also be formed *via* an intermolecular hydrogen abstraction from the β-carbon of the dead polymer. Methyl and ethyl branches having tertiary carbon can be formed by head-to-head addition and subsequent Cl shifts and propagation. 2-chloroethyl and 2,4-dichloro-n-butyl branches are formed by intramolecular abstraction of hydrogen from a backbone CHCl moiety (back-biting reaction) and subsequent head-to-tail propagation.[22] Depending on the position of a radical, the resultant branches can be attached to a carbon atom which has either tertiary hydrogen or tertiary chlorine atom.[19] Further details on these reactions, especially historical aspects of their discovery, can be found in the review papers.[23,24]

The first data on branching came from studies of the viscosity of PVC solutions[25] and GPC.[26] One can easily understand that these methods can give only very approximate results, and hence further studies were conducted to find possible application of spectral methods in quantitative determination of the number of branches in PVC. Two methods of polymer preparation for direct observation by spectral methods are used. These methods include PVC reduction, either by $LiAlH_4$[28-33] or by Bu_3SnH, as proposed by Starnes.[27] Reduction by $LiAlH_4$ is incomplete, requires long reduction time (1–3 weeks), and produces undesirable side reactions; therefore, the Bu_3SnH reduction is used more frequently. Reduced PVC is further studied by ^{13}C NMR using methods developed for polyethylene. Historical details on development of the methods of study can be found in a review

paper.[24] The concentrations of different types of branches are given in Table 1.6 based on the available literature.

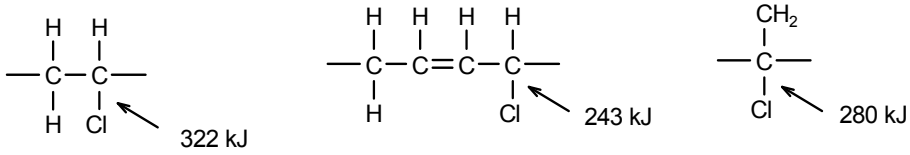
Table 1.6. Branches in PVC

Irregular segment	Concentration in number of groups per 1000 VC mers	Refs.
chloromethyl branch (tertiary H)	3.3-4.8	18
chloromethyl branch	3.0-4.8	34-36
1,2-dichloroethyl branch	0.14-0.55	18
ethyl branch	0.1-0.55	35-36
2,4-dichloro-n-butyl branch	0.5-1.7	18
butyl branch	0.5-1.7	35-36
short chain branch	0.8	37
long chain branch (tertiary Cl)	0.07-0.14	18
long chain branch (tertiary H)	0.03-0.07	18
long chain branch	0.1-0.2	18, 35-37

1.4.2 TERTIARY CHLORINE

Table 1.6 and discussion in the previous section show that some concentrations of tertiary chlorine are present and that they may come from ethyl (only in PVC synthesized at elevated temperature), butyl, and long branches as is commonly accepted. Considering that long branch concentration is usually low, most tertiary chlorine comes from butyl branches.[44] The 1-2 intermolecular hydrogen shift would result in a fraction of the methyl branches carrying a tertiary chlorine, and they may therefore be more significant for the thermal stability of PVC (especially at high monomer conversions) than was described earlier.[19]

Rogestedt and Hjertberg have studied branched structures and they concluded that out of all tertiary carbons only 2-2.5% are associated with chlorine.[35-36,38] In their extensive studies of tertiary chlorine, their concentration was estimated to be between 0.7 and 2.1 groups per 1000 VC.[36] The energy of C-Cl is given below:[37]



It is pertinent from this comparison that lower energy is required to break a chlorine bond with tertiary carbon as compared to secondary carbon. But, allylic chlorine bond is still easier to break. At the same time, it should be noted that concentrations of tertiary chlorine are usually larger than the concentrations of allylic chlorines. For this reason the influence of tertiary carbons on degradation rate is believed to be prevalent.[35,37] The enthalpy

required for reaction to occur is larger for chlorine attached to the secondary carbon (195 kJ/mol) than tertiary carbon (174 kJ/mol).[39]

Experimental studies show that if the content of allylic and tertiary chlorine is eliminated by reaction with trialkylaluminum or tin derivatives, PVC has a decreased rate of degradation.[40] Hjertberg *at al.* regard tertiary chlorine to be the most important defect of PVC synthesis from the point of view of its impact on PVC thermal degradation.[41] Studies on synthesis by Hamielec *et al*.[42] lead to the same conclusion based on a good correlation between degradation rate and concentration of tertiary chlorine.

The concentration of tertiary chlorines increases with an increase in monomer conversion beyond critical conversion (~60%). At the same conversion level, the concentration of tertiary chlorine atoms increases with an increase in polymerization temperature.[42]

The theoretical investigation of PVC structural irregularities, using MNDO and AM1 calculations, show that chlorine atoms bound to the tertiary carbon atoms are responsible for the low thermal stability of PVC.[43]

1.4.3 UNSATURATIONS (END CHAIN – VINYL, IN-CHAIN – VINYLENE)

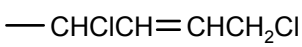
The presence of internal double bonds in PVC has been studied by UV and Raman spectrophotometry, ^{13}C NMR, ^{1}H NMR, and degradative methods. It is important for these studies to evaluate the quantity of the double bonds present in polymers, but it is also expected that single internal double bonds, sequences of conjugated double bonds, double bonds in conjugation with oxygen-containing groups, and double bonds at chain ends can be determined separately.

Several methods can be used to study the unsaturated structures present in PVC. The main method is based on bromination, which gives the total number of double bonds present in polymer. Ozonolysis, in turn, coupled with molecular weight change determination, gives the number of double bonds which are internally present in the polymer chain. The difference in reading gives double bonds at the chain ends. Numerous investigators have studied the chemical structure of chain ends. The most often applied technique is based on the ^{1}H NMR method.

Petiaud[45] and Schwenk[46] were able to record signals assigned to the following structures:

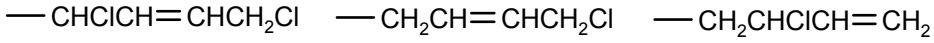
Caraculacu,[47] using Fourier transform ^{1}H-NMR, found a series of five signals, three of which were assigned to the following structures:

Hjertberg[48] confirmed the presence of Schwenk's structure:

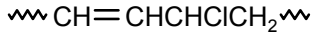


and found that the other groups included at chain ends contain saturated groups: –CHCl-CH_2Cl and $–CH_2CH_2Cl$. The presence of all these groups was discussed by Braun.[49]

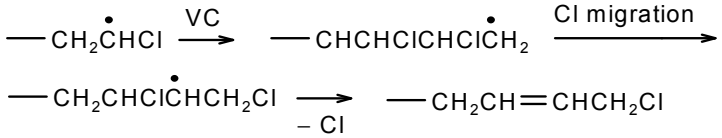
The following chain-end unsaturations are recognized:[21]



This indicates that about 30 years ago unsaturation structure was well predicted. The following is the chemical structure of the internal double bond:[21]



Hjertberg[48] showed the probable pathway of their formation, which is given by the following equations:



The same mechanism is proposed today to explain formation of chain-end double bond and allylic chloride at the chain end.[21] The end-group with methylene ($CH_2CHClCH=CH_2$) is formed by chain transfer reaction to VC.[21] Internal allylic chlorine is the result of intermolecular chain transfer to polymer.[50]

Conformation of chain is essential for the degradation reaction. The propagation reaction is a 1,4-dehydrochlorination which proceeds through a six atom transition state that requires a *cis*-(chloroallylic) system with a planar conformation of CHCH=CHCC1. The restricted conformation can be more easily achieved at the surface of PVC primary particles than in their interior, because of higher conformational mobility. This means that PVC degradation should start and take place primarily at surfaces of primary particles.[51] In conclusion, *cis*-allylic chlorides eliminate HC1 much faster than do *trans* isomers.[51]

The number of internal and total double bonds was estimated by various authors in the following wide range:

Table 1.7. Unsaturations in PVC

Source	Double bonds per 1,000 monomer units	Year
Internal allylic chlorine		
Hjertberg[41]	0.1-0.2	1988
Endo[21]	0.1-0.3	2002
Van Cauter[18]	0.0-0.6	2007
Allylic end-group		
Purmova[19]	0.46	2005
Van Cauter[18]	0.45-0.95	2007
Allylic chlorine		
Dean[52]	0.53-0.72	1988
Jian[53]	0.056-0.40	1990
Xie[54]	0.05-0.07	1994

Table 1.7. Unsaturations in PVC

Source	Double bonds per 1,000 monomer units	Year
Internal unsaturations		
Abbas[29]	4	1975
Michel[55]	0.05	1975
Minsker[56]	0.09-0.27	1980
Guyot[20]	0.1-0.3	1986
Bensemra[57]	0.24-0.52	1989
Xu[58]	0.137-0.18	1989
Jian[53]	0.196-0.98	1990
Rogestedt[36]	0.07-0.9	1993
Veronelli[59]	0.58	1999
Purmova[19]	0.42	2005
Unsaturated end-group		
Guyot[20]	0.75	1986
Xu[58]	2.58-3.2	1989
Bensemra[57]	0.75-0.8	1989
Endo[21]	0.75	2002
Total unsaturations		
Zilberman[60, 61]	1.4-3.4	1972, 1975
Boissel[62]	1.5-3	1977
Minsker[63]	>5	1981
Rabek[64]	0.5-2.5	1985
Dean[52]	2.4-3.5	1988
Xu[58]	2.8-3.3	1989
Bensemra[65]	1.6-2.3	1989
Jian[53]	7.3-8.7	1990

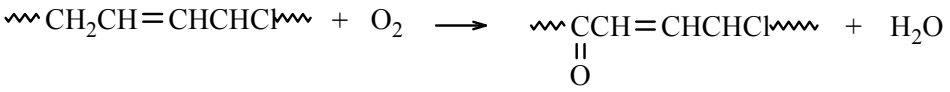
There is a broad range of determined values. This may not be surprising because data are frequently determined for polymers which for experimental reasons were polymerized under conditions quite different than those used in production of commercial polymers. Also, the data span for 35 years, during which many improvements were made to polymer quality.

Double bonds are not known to affect dehydrochlorination but allylic structures do. Minsker[63] claims that unsaturations at the chain ends had no effect on polymer thermal stability because they immediately become oxidized to ketoallylic groups. This opinion does not have a lot support among researchers (see more on this subject in the next section).

1.4.4 OXYGEN CONTAINING GROUPS

1.4.4.1 Ketochloroallyl groups

Minsker[66,67] proposed that allylic chlorine does not exist in normal polymer because it is immediately oxidized during production, drying, and storage to form:



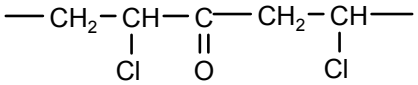
Caraculacu[68] found that 4-chlorohexene-2 and 2-chlorohexene-3 were not oxidized to ketoallylic structures even after 1 year at room temperature. Braun[69] found that keto groups in alpha position to allylic chlorine decrease their rate of degradation rather than increase it because of their electron withdrawing character.

Minsker[66] shows that ketochloroallyl groups are at concentrations of 0.1/1000 VC which is below the detection limits of ^{13}C NMR.[70] For this reason, in a dedicated study[70] the presence of ketochloroallyl groups could not be confirmed. At the same time, it was found that spray drying produces these groups only if PVC is dried without prestabilizer. Drying in a laboratory oven required at least 50 h exposure to 50°C to detect the presence of some groups which could increase initial degradation rate.[70]

Minsker[66] suggested that the ketochloroallylic groups are 100 to 1000 more reactive than chloroallylic groups and for this reason they are predisposed to act as initiation centers. It is a correct way of reasoning, but at the same time it should be considered that they are in such low concentration that even if they were proven to be present in commercial PVC, their impact on the PVC degradation rate would have been minimal.

1.4.4.2 α- and β-carbonyl groups

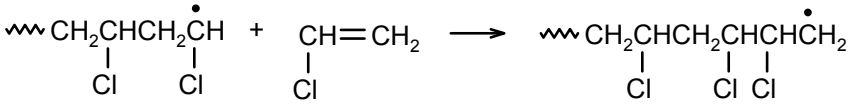
If a C=C bond can weaken a C-Cl bond in the β-position, the same effect should be expected when a double bond is formed between the carbon atom and oxygen. The possibility of these groups serving as initiation centers for dehydrochlorination was discussed by Bauer[71] and George.[72] Svetly[73] suggested that the initiation reaction proceeds through a cyclic transition state. Braun demonstrated that carbon monoxide can copolymerize with vinyl chloride, leading to unstable structures, as follows:



1.4.5 HEAD-TO-HEAD STRUCTURES (1,2-DICHLORO GROUPS)

It is thought that the PVC chain consists mainly of a head-to-tail arrangement of monomer units. The first studies on irregular structures were conducted by Canterino,[74] Bailey,[75] and Murayama,[76] who obtained head-to-head PVC by chlorination of 1,4-polybutadiene. The reaction used for synthesis of head-to-head PVC was later studied by several researchers.[77-81]

The following is the chemical reaction of head-to-head structure formation:[21]



The propagation reaction is an important elemental reaction to determine molecular weight and structural defects. Monomer can add onto the polymer chain in two ways: head-to-head or head-to-tail but it grows mainly by head-to-tail addition.[21] The activation energy of head-to-head addition is 6.28 kJ/mol higher than head-to-tail addition. The propagating radicals produced by head-to-head addition induce 1,2-chloro-atoms migration followed by addition of VC, leading to the formation of chloromethyl branches.[21]

Table 1.8 shows the frequency of head-to-head addition as determined by various researchers

Table 1.8 Head-to-head structures in PVC

Source	Head-to-head structures per 1,000 monomer units	Year
Mitani[82]	6-7	1975
Schwenk[83]	8	1979
Rabek[64]	6-7	1985
Endo[21]	6.4-6.9	2002

Table 1.8 shows that there is a good agreement between different sources.

Murayama[76] showed that head-to-head PVC degrades at a lower temperature than the head-to-tail form, which was also confirmed by Crawley.[81]

1.4.6 INITIATOR RESTS

Selection of initiator affects the reaction rate, molecular weight, morphology of PVC particles, uniformity of polymerization reaction, and thermal stability of resultant polymer. Bulk, solution and suspension polymerization use monomer soluble initiators, unlike emulsion polymerization, which uses a monomer insoluble initiator.

Initiator is usually selected in such a manner that it has about 1 h half-life under reaction conditions (formulation, temperature).[84] For typical suspension and bulk initiators, the temperature of half-life varies in the range of 54-80°C.[84] Chemical structures and basic properties of main commercial initiators can be found elsewhere.[84] A single initiator is seldom used in commercial polymerization. Commercial formulations usually use 2-4 different initiators. The most reactive initiator is used to begin polymerization and when it is exhausted, the next initiator takes a leading role. Peroxydicarbonate is commonly used as the primary initiator.[84] A typical formulation will use 0.03 to 0.08 parts of initiators per 100 parts of vinyl monomer.[84]

The method of addition of initiator has a great effect on PVC particle uniformity as well as the size distribution.[21] If initiator is dissolved in monomer, polymer particles are more uniform than if initiator is predispersed in a continuous phase of suspension polymerization medium. This shows that diffusion of initiator into monomer droplets is time-

controlled.[85] Composition of polymerizing mixture may affect also other morphological features such as particle size distribution and porosity.

Morphology, especially porosity, is a factor in dehydrochlorination because it affects diffusion of hydrogen chloride – a catalytic product of dehydrochlorination. Also, molecular weight and its distribution affect dehydrochlorination. In addition, initiator rests remain as a part of polymer composition. It is proposed that initiator rests may dissociate, as a result of which a free, low molecular radical is formed.[86] This radical is mobile and thus may participate in initiation of dehydrochlorination. Effect of initiator rests is also explained by polaron formation from the eventual oxidoreduction reaction of polyene sequences by residues of initiators.[87] Depending on the selected initiator, more or less irregular segments are produced, and this affects dehydrochlorination.[88]

It was estimated that about 20% chain ends are formed by initiator ends.[65] This is in line with the mechanism of polymerization because initiators begin a chain of polymer reactions with involvement of monomer which is more likely to react due to its higher concentration in reaction mixture. Initiator may also end a reaction chain by reacting with a microradical, and this produces initiator rest in the chain ends. Table 1.9 gives concentration of initiator rests from literature data.

Table 1.9. Initiator rests in PVC.

Source	Initiator rests per 1,000 monomer units	Year
Guyot[89]	0.8	1986
McNeill[90]	0.2-0.25	1995
Endo[21]	0.14-0.4	2002
Van Cauter[18]	negligible	2007

Direct data on influence of initiators on dehydrochlorination are limited. Azo-bis(isobutyronitrile) was found to give less stable polymer than bis(4-t-butylcyclohexyl)peroxydicarbonate.[91] Initiator residues also affect early color of polymer most likely due to increased defect structures.[50] Unreacted initiator was more detrimental for PVC thermal stability because it was able to abstract hydrogen from polymer chain, which initiated chain reactions.[50]

1.4.7 TRANSFER AGENT RESTS

2-mercaptoethanol is a popular chain transfer agent for manufacture of PVC of lower molecular weight.[92] Other transfer agents include: dodecylmercaptan, α-thioglicerol, and thioglycolicacid.[93-94]

1.4.8 DEFECTS INTRODUCED DURING PROCESSING

Considering that the entire book is devoted to the formation (and prevention of) of defects during various types of processing, we will only acknowledge the problem here as opposed to an exhaustive discussion.

Any form of degradation produces HCl, and as a result, a system of isolated and conjugated double bonds. The presence of these bonds changes electron distribution along the chain and invites oxidative reactions which produce hydroperoxides and eventually carbo-

nyl groups. These are especially essential in UV degradation processes because they promote UV absorption and related photodegradative changes.

From the mechanism of stabilization it is also pertinent that some stabilizer rests may be substituted into the polymer chain using available double bonds formed during degradation. Labile chlorine atoms may be removed by some stabilizers. All these reactions will increase stability of polyvinylchloride, but in the majority of cases, processing will increase the degradation rate of thermal and radiative processes because of increased concentration of defect structures capable of stimulating degradative processes.

1.4.9 PVC HAVING INCREASED STABILITY

Minsker and Zaikov[95] put forward an argument that future research should concentrate on the PVC production to develop a polymer which will have fewer (or even none) labile structures and require less additives for its processing. According to authors of this concept, it will increase number of applications of PVC and remove some health and environmental concerns. The basic proposed solutions are as follows:

- Manufacture of an industrial PVC, that does not contain labile groups. This will provide a drastic increase of its intrinsic stability, the possibility of processing PVC with minimal concentrations (or total absence) of stabilizers
- Wide use of the latest achievements in the area of PVC degradation and stabilization to permit formulation of rigid, semirigid, and flexible materials with minimal contents of chemical additives and increased service lifetimes
- Development of safe and environmentally friendly additives.

This is an excellent recapitulation of this chapter and good strategy for future research which will aim at easier polymer processing. At the same time, it is realistic to expect that in the foreseeable future we will need to deal with materials that we know today; therefore the task at hand would be to use our knowledge more efficiently to achieve some of these goals now.

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2

PVC Manufacture Technology

2.1 MONOMER

Vinyl chloride is the sole monomer used in the production of PVC. Its structure and properties are given in Table 2.1.

Table 2.1. Typical properties of vinyl chloride

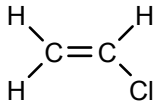
Property	Description
General	Vinyl chloride is a flammable, colorless gas with a sweet odor at room temperature. It is mainly used for production of PVC but also as a refrigerant and comonomer
Chemical structure	
Chemical formula	C_2H_3Cl
IUPAC name	1-chloroethene
Alternate names	chloroethylene, chloroethene, ethylene monochloride
Identifiers	CAS # – 75-01-4; EINECS – 200–831–0; UN # – 1086; RTECS – KU9625000
Molecular weight, g/mol	62.5
Odor	mild, sweet
Color	colorless
Melting point, ^oC	-153.8
Boiling point, ^oC	-13.37
Decomposition temperature, ^oC	450
Flash point, ^oC	-78
Autoignition temperature, ^oC	472
Explosive limits in air, vol%	3.6 and 33
Density, kg/m^3	2.56 (gas); 908.41 (liquid)
Vapor density (air=1)	2.15
Vapor pressure at 25^oC, mm Hg	2600

Table 2.1. Typical properties of vinyl chloride

Property	Description
Solubility in water, wt%	0.95
Solubility of water in 100 g VC, ml	0.08 (20°C)
Solubility in solvents	alcohol, ether, carbon tetrachloride, benzene
Henry's law constant, atm m^3/mol	2.71E-02
Critical temperature, °K	432
Critical pressure, MPa	5.67
Enthalpy of vaporization, kJ/mol	21.998-23.3
Enthalpy of fusion, kJ/mol	4.92
Enthalpy of formation, kJ/mol	28.45
Specific heat capacity, J/kg/g	0.8592 (gas), 0.9504 (solid)
Heat capacity of liquid at 298.15K, J/molK	0.053625
Latent heat of vaporization, kJ/kg	333
Antoine equation parameters	A – 3.98598, B – 892.757, C – -35.051 (165.2-259.3K)
Octanol/water partition, $\log K_{ow}$	1.36
Odor threshold, ppm	3000
Half-life in air, h	few

2.2 BASIC STEPS OF RADICAL POLYMERIZATION

2.2.1 INITIATION

Vinyl chloride has low reactivity but its radical is highly reactive. For this reason, PVC is manufactured by radical polymerization. Initiation is a two step process, as given by the following reactions:

$$I \longrightarrow 2\dot{I} \quad \text{(I - initiator)}$$

$$\dot{I} + M \longrightarrow R^{\bullet} \quad \text{(M - monomer; } \dot{R} \text{ - growing polymer radical)}$$

First, the initiator produces free radicals which then react with monomer, forming a radical ready for the next step – propagation.

This method of initiation causes the chain end structure of PVC macromolecules to consist of initiator fragments.

Initiators are important components of industrial polymerization formulations. Table 2.2 shows chemical structures of the most common representatives with their half-life temperatures, HLT.

Table 2.2. Examples of common initiators[1,2]

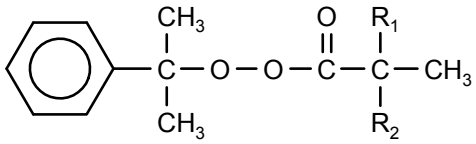
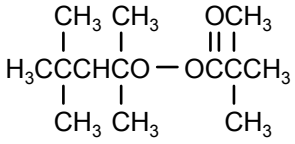
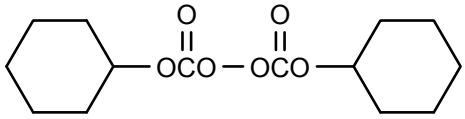
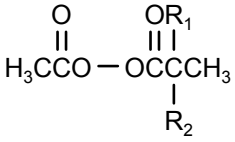
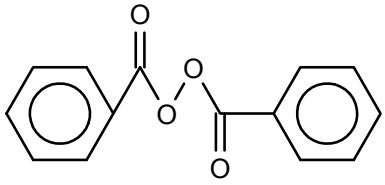
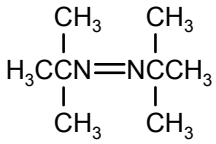
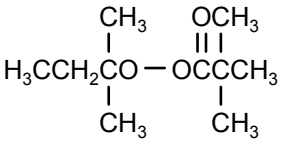
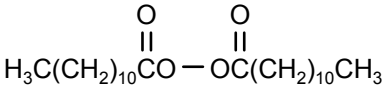
Name	Abr.	HLT, °C	Chemical formula
Cumyl peroxyneodecanoate	CUPND	55	
tert-Octyl peroxyneodecanoate	TOPND	56	
Dicyclohexyl peroxydicarbonate	CHPC	57	
tert-Butyl peroxyneodecanoate	TBPND	64	
Benzoyl peroxide	BPO	65	

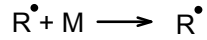
Table 2.2. Examples of common initiators[1,2]

Name	Abr.	HLT, °C	Chemical formula
2,2'-azobisbutylnitrile	AIBN	73	
tert-Amyl peroxypivalate	TAPPI	74	
Dilauroyl peroxide	LP	80	

Selection of initiator influences the molecular weight of polymer and the polymerization rate. The molecular weight is controlled by chain transfer to monomer and propagation rate. If the temperature of polymerization increases, the rate of chain transfer to monomer will be higher than the propagation rate. The higher the temperature, the lower the molecular weight. For PVC resins having K=70 and above, the polymerization temperature should be below 52°C. Initiators having HLT about 57°C are used as primary initiators. To boost the slow initial rate, initiators having HLT lower than 57°C are used. Less active initiators (TAPPI to LP) are used as secondary initiators in production of PVC grades below K=60.

2.2.2 PROPAGATION

The propagation reaction can be schematically written as



Addition of monomer increases molecular weight of the growing radical, which continues to react according to the same scheme. Vinyl chloride may add onto the polymer chain in two ways: head-to-head and head-to-tail. The head-to-tail addition prevails. But in some cases head-to-head structures are formed which contribute to the defect formation similar to any other anomaly of polymerization reaction, which result in other typical chain defects as discussed in Chapter 1.

From the point of view of polymerization conditions, defects are formed with increased incidence at high monomer conversions (above 60%).

Polymerization rate is almost independent of initiator concentration because the presence of polymer in the reaction mixture exerts a catalytic effect, promoting further polymerization. The catalytic effect of polymer is proportional to its actual surface area. The propagation rate constant, k_p, is given by the following equation:[1]

$$k_p = 3.3 \times 10^6 \exp\left\{-\frac{3700}{RT}\right\} \qquad [2.1]$$

where:

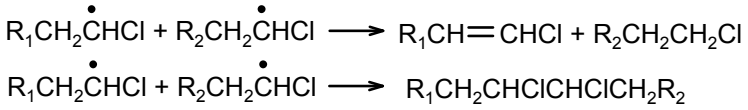
R gas constant
T absolute temperature.

This equation confirms the previous statement that initiator concentration does not enter the relationship, which is only controlled by temperature.

The rate of polymerization is not uniform throughout the mixture because it is higher inside a swollen particle of polymer. This is most likely due to the catalytic effect of polymer and reduction of radical termination rate because of reduced mobility of the growing radical. The rate of polymerization is thus auto-accelerating, which, in combination with its high exothermic effect (106 kJ/mol), puts emphasis on effective cooling which controls the process rate and quality of the product.

2.2.3 TERMINATION

Termination occurs by disproportionation and combination, as shown by the following reactions:



The rate constant of termination, k_t, is expressed by the following relationship:

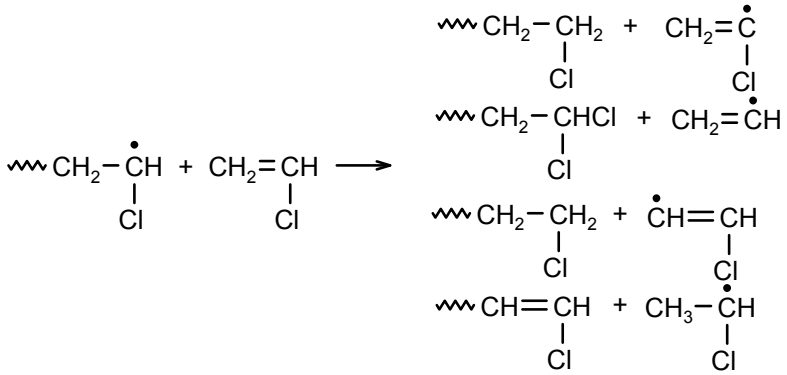
$$k_t = 1.3 \times 10^{12} \exp\left\{-\frac{4200}{RT}\right\}$$

The ratio of disproportionation to combination is difficult to determine but the combination is known to be a prevalent mechanism of termination.[1,5]

One peculiarity of PVC polymerization is that polymer is not soluble in its monomer and it precipitates when formed. Monomer is capable of swelling polymer, which results in a porous structure of polymer grains formed, as well as the possibility that reaction of polymerization continues in a portion of monomer used for swelling the already formed grains. This gives PVC peculiar morphological structures which can be manipulated by process.

2.2.4 CHAIN TRANSFER TO MONOMER

A growing radical may react with monomer, forming polymer and a monomer radical, which further grows, due to reaction with monomer. These reactions, called chain transfer reactions, may occur according to one of the schemes below:[1]



The third reaction scheme is considered to be the main reaction of a new radical generation based on activation energies of reactions.[1]

Chain transfer constant for PVC is given by the following equation:

$$C_m = 125 \exp\left\{-\frac{7300}{RT}\right\} \qquad [2.2]$$

The values of C_m are large due to the high reactivity of vinyl chloride. This reaction controls the molecular weight of polymer. With temperature of reaction increasing, the value of constant increases, which results in an increased number of chain transfers and lower molecular weight of the resultant polymer.

Chain transfer to polymer results in formation of long branches as discussed in Chapter 1.[3]

Various chain transfer agents, such as dodecylmercaptan, 2-mercaptoethanol, α-thioglycerol, or thioglycolic acid, may be used to decrease molecular weight of the resultant polymer.[4]

2.3 POLYMERIZATION TECHNOLOGY

PVC production has grown by about 4% per year since 1990. The largest growth is experienced in Asia (especially in China), followed by North America and Europe.[6] There are four major methods of production of PVC, including bulk, emulsion, solution, and suspension polymerizations. Suspension polymerization is the most common since it accounts for 80% of world production of PVC (75% in USA and 93% in Japan).[6] It is followed by production of paste-type resins by emulsion (12% in the world) and microsuspension polymerization (3% USA and 5% Japan). Bulk polymerization contributes 8% of world production of PVC. Solution polymerization is not a commercial scale method.

2.3.1 SUSPENSION

Suspension polymerization is a batch process which includes four unitary operations:

- polymerization
- stripping residual vinyl chloride
- centrifugation of water suspension to remove water
- drying.

The typical formulation of reactor charge is given in Table 2.3.

Table 2.3. Typical formulation for suspension polymerization.[6]

Component	Concentration, parts
Vinyl chloride	100
Demineralized water	120
Suspending agent	0.05-0.1
Initiator	0.03-0.16

Types of initiators used are presented in Table 2.2 and their role is discussed in the previous section. A suspending agent (frequently called a protective colloid) prevents agglomeration of vinyl chloride droplets changing later into sticky particles of formed polymer. Without a suspending agent, uniformity of suspension will suffer and particle size will have a very broad range, with large lumps which will diminish the quality of PVC. Water soluble natural and synthetic polymers are known to prevent coalescence of droplets and agglomeration of particles. Partially hydrolyzed polyvinyl acetate (polyvinyl alcohol) and hydroxypropyl methylcellulose are the most popular suspension agents. Two types of commercial products are used: primaries and secondaries.[6] Primaries, which have a degree of hydrolysis in the range of 71 to 82%, are used to control particle size of PVC. Secondaries, which have a degree of hydrolysis in the range from 45 to 57%, are known to increase porosity. Depending on application and, thus, required morphology, different combinations of both suspending agents are used. It is quite obvious from formulation that suspension PVC contains limited amounts of additives which may complicate its further processing and its thermal and UV stability.

Polymerization is performed in large reactors (usually having a volume of up to 200 m^3). Considering that vinyl chloride is carcinogenic, most reactors are operated without opening. Several hundred batches can now be run without opening the reactor. This is due to excellent coating which prevents deposition of reacting mass on the reactor walls. It is also very important to control the temperature of reaction which is exothermic. The rate of heat removal is usually the rate controlling factor.

After reaction is complete, walls of the reactor are rinsed with water to remove any particles. If such particles are left in the reactor for the next batch, a monomer will be absorbed by them and polymerized within particles, resulting in non-porous particles which will cause formation of so-called “fish-eyes”. In addition, these particles will hold more vinyl chloride and increase its residual concentration in the final product. The reactor is coated with adhesion-preventive compound before a new batch begins. The reactor is charged again and reaction mixture is brought to a desired temperature to begin a new

polymerization. Initiator used in suspension polymerization is monomer-soluble (unlike in emulsion polymerization, where it is water-soluble).

In the next operation, reaction mixture is stripped free of monomer to at least below 1 ppm. For a good stripping performance, polymer grains must be porous. In modern plants, steam stripping columns are used. In older plants, stripping is done directly in the polymer vessel or in the tank into which slurry is transferred after polymerization. The stripping temperatures exceed 100^{o}C. The typical process time does not exceed 3 min. Holding polymer for longer times may cause its degradation and yellowing. The monomer recovered from this process is reused for the production of polymer.

Monomer-free slurry contains more than 50% water which is removed by centrifugation during which at least 60% of the water is removed. The effectiveness of water removal depends on the slurry temperature. At temperatures above glass transition temperature of PVC (82^{o}C), more water is removed, most likely because the more elastic grains permit water removal from pores and interstices. Before transfer to dryer, antistatic is frequently added to prevent static formation during drying and resin use.

The most common dryers are a fluidized bed (for major grades) and rotatory (for shorter runs). Until moisture is present, temperature is below 100^{o}C because heat is utilized for water evaporation. Close to moisture removal, temperature rises. Moisture removal is strictly controlled because a too large concentration of moisture may cause bubbling during processing, whereas too low moisture means longer exposure to higher temperature which may cause degradation and an increase in static formation, causing particles to stick to each other. Before PVC is packaged, it is screened in order to remove too large particles.

The above description of the process shows that there are several points where quality of polymer may be affected so as to influence its future thermal and environmental stability. These include:

- effect of initiator type and concentration
- effect of polymerization temperature on molecular weight and polydispersity
- total conversion of monomer (defects types and their concentrations)
- selection of suspending agent(s) (particle size and porosity and thus conditions of stripping, centrifugation, and drying)
- size of polymerization reactor (ease of cooling which affects efficiency and molecular weight and its distribution)
- reactor wall coating and rinsing efficiency (concentration of particles, which cause fish eye defects)
- stripping temperature and duration (affect color and stability of resin)
- temperature of centrifugation (higher temperature increases effectiveness of centrifugation and thus reduces PVC exposure to heat)
- selection of dryer and its operating conditions (length of polymer exposure to elevated temperature)
- residual moisture level (potential bubbling, thermal degradation, antistatic properties).

Some of these influences (formation of defects) were already discussed and others are discussed in the next chapter.

Near infrared spectroscopy was applied for monitoring of suspension polymerization process.[7] Use of calibration models permitted to predict and control the morphological properties of manufactured polymer by in-line monitoring.[7] The bulk density, the cold plasticizer absorption, and the average particle diameter were controlled.[7]

Morphological properties of suspension PVC were influenced by operation of condenser.[8] Delay in reflux operation increased cold plasticizer absorption, and decreased bulk density and K-value.[8] The commencement of refluxing before 20% conversion caused formation of bimodal particle size distribution (monomodal particle size distribution was obtained for longer delays).[8] This shows that operation principles have strong influence on properties of suspension PVC.[8]

Increase of final temperature of reaction and injection of additional reactant increased production output of suspension PVC by 19.1% without influence on resin quality.[9] This was accomplished by careful control of pressure and temperature in the reactor, and control of process variables.[9]

2.3.2 PASTE RESIN MANUFACTURING PROCESSES

Emulsion polymerization is the leading process of manufacture of paste-grade PVC. Microsuspension polymerization is also used for this purpose. We will briefly discuss both processes to show differences in technology and outcome. In the process technology, these two methods differ in the polymerization process, with all other unitary operations being the same.[6]

Paste grade producing plants are smaller and they are required to produce larger number of grades. Also, reactors are much smaller (20-80 m^3). The Huels plant having reactor with capacity of 200 m^3 is the only known exception.[6]

Unit operations include:

- charging, premixing, and homogenization (only microsuspension polymerization)
- charging and polymerization
- stripping
- spray drying
- separation, grinding, screening, and packaging.

Table 2.4 compares typical formulations for emulsion and microsuspension polymerizations.

Table 2.4. Typical formulations for microsuspension and emulsion polymerizations.[6,10]

	Concentration, parts	
	microsuspension	**emulsion**
Vinyl chloride	100	100
Water	137	110-180
Oils soluble initiator	0.2	-
Water-soluble initiator	-	1-1.2
Emulsifier	1	1-2

In microsuspension polymerization a mixture of vinyl chloride, water, emulsifier (e.g., alkyl aryl or alkyl sulfonate), and monomer-soluble initiator (e.g., lauroy peroxide) is homogenized in a separate vessel and pumped into the reactor. The mixture is then heated with agitation to the polymerization temperature. A stable emulsion with particle size of 0.1-5 μm is formed. This is in contrast to suspension or bulk polymerization which produces much larger particles (100 μm and above). Microsuspension polymerization differs from emulsion polymerization in the type of initiator used (oil or water soluble, respectively) and an additional operation used in microsuspension (homogenization), which is required to obtain regular, small particles.

In the case of emulsion polymerization, reaction begins in a water phase taking advantage of the fact that vinyl chloride is slightly soluble in water. Typical initiators of emulsion polymerization are ammonium and potassium persulfates and hydrogen peroxide. Polymerization continues in the monomer phase because polymer is not soluble in either monomer or water but monomer is very soluble in polymer (30 wt% monomer can be absorbed by polymer). Good control of particle size due to the use of proper mixing and effective emulsifier permits production of PVC with very narrow particle size distribution. Frequently, emulsion polymer is mixed in a production plant with microsuspension polymer which has a much broader particle size distribution. By such premixing, an adequate proportion of various particle sizes can be achieved in order to obtain a maximum packing density of polymer which reduces plasticizer demand (and viscosity) of PVC plastisols.

In the emulsion polymerization, the type and the quantity of emulsifier is the most crucial feature of the process which impacts particle size distribution of the resultant resin. Usually anionic emulsifiers are used and their concentrations are high compared with relatively pure suspension polymerizates. Unlike in other types of polymerization, emulsifier may not be added at the beginning but is metered throughout the process to control the rate of initiation and the size of particles (if more surfactant is added, more new growth sites are formed and particles become smaller). The rates of polymerization can be increased by the addition of reducing agents which increase the rate of initiation and help in reducing polymerization temperature.

Particle size distribution of emulsion polymerization can be further controlled by the so-called seeded emulsion polymerization. By choice of size and number of seed latex, the number of growth sites (particles) is controlled, giving superior control over particle size

distribution. If combination of large and small particles is required, this is usually achieved by the use of a blending tank in which latices of different particle sizes are mixed prior to drying.

The polymerization reactor is protected against deposition of particles either by composition (glass lining or use of stainless steel reactors) or by a protective coating similar to suspension polymerization. Conversion of monomer for both microsuspension and emulsion polymerization is in the range of 80-90%. In the next step, reaction mass must be stripped of vinyl chloride. This is done by a combination of vacuum and temperature, most frequently in a reaction vessel but also in special tanks, columns, or thin film evaporators. If the temperature of the process is higher than the glass transition temperature of PVC (82^{o}C), polymer will begin to degrade. A slurry stripped to at least 8.5 ppm of vinyl chloride is transferred to dryer.

Slurry is pumped to a spray dryer where it is atomized into fine droplets falling into hot air. The selection of drying temperature (inlet and outlet temperatures) is important for quality since PVC without thermal stabilizers can be degraded and also agglomerated (if temperature is close to the glass transition temperature). The resin agglomeration also depends on atomizer tip speed. Atomizers are either equipped with a spinning disc or nozzle.[6] The performance of atomizer controls the size of the latex droplet and combination of inlet and outlet temperature and atomizer tip speed controls percentage of agglomerates. Higher atomizer tip speed produces a higher percentage of coarse particles. Inlet temperature increase causes an increase in the amount of agglomerates because more particles become fused. Similar effect has an increase in outlet temperature. Fine particles of paste resin tend to lump and cake, and for this reason bag shipment is more frequently used than bulk transportation.

The above description of the process shows that there are several points where quality of polymer may be affected so as to influence its future thermal and environmental stability. These include:

- effect of initiator type and concentration
- effect of polymerization temperature on molecular weight and polydispersity
- total conversion of monomer (defects types and their concentrations)
- type and quantity of emulsifier
- size of polymerization reactor (ease of cooling which affects efficiency and molecular weight and its distribution)
- reactor wall coating and rinsing efficiency (concentration of particles, which cause fish eye defects)
- stripping temperature and duration (affect color and stability of resin)
- inlet and outlet temperatures in spray dryer
- atomizer tip speed (influences time of exposure to elevated temperature).

Some of these influences (formation of defects) were already discussed and others are discussed in the next chapter.

2.3.3 BULK

Developed by Saint Gobain, later Rhone-Poulenc, and now Arkema (Lacovyl), the bulk (or mass) polymerization is the simplest process which uses only vinyl chloride monomer and initiator.[6] It does not require preparation of solutions, water, drying, separation, and waste water treatment. It is very efficient process, which, conducted in a small reactor, yields a large production output. It also results in the purest polymer because of simple polymerization formulation.

There are also many disadvantages, such as

- long heating required to strip residual monomer
- difficulties in cleaning off-gases (steam and/or nitrogen) from residual monomer
- problems with efficient wall coating and thus batch process is required
- production of fine particles which are difficult to handle
- complicated, two-stage process.

The last disadvantage is caused by the fact that during polymerization the reaction mixture changes from liquid to solid and it needs different conditions of mixing. The first commercial process in 1939 used a single reactor but sine 1962, two reactors are used: pre-polymerizer and post-polymerizer. In the pre-polymerizer, reaction is conducted up to 10% conversion, and in the post-polymerizer, up to 80% conversion of monomer. Since the first stage process is more efficient (reaction takes only 20 min), one pre-polymerizer is serving several post-polymerizers (initially horizontal but from 1978, vertical reactors).[6] Reaction temperature at the first stage is higher (usually 60-70^{o}C) than in the second stage (usually 50-60^{o}C). Initiators for the first and the second stage are different, considering temperature difference. The first stage produces seed particles and therefore controls particle morphology. The higher reaction temperature increases aggregation. Aggregation is also controlled by the type and quantity of initiator added in the first stage. Also, agitation speed helps to control primary particle size. The temperature of the second stage is selected to control molecular weight of the product. Second stage initiators have longer half-life time. Usually a combination of 2-3 initiators is used to obtain constant temperature of reaction. Material becomes powdery at about 20-25% conversion.[6] Final conversion of monomer is very important for porosity of particles. A high conversion rate will cause densification of particles and reduction of porosity.

The above description of the process shows that there are several points where quality of polymer may be affected so as to influence its future thermal and environmental stability. These include:

- effect of initiator type and its concentration in each stage of polymerization
- effect of polymerization temperature on molecular weight and particle size
- total conversion of monomer (defects types and their concentrations)
- reactor wall coating and cleaning efficiency (concentration of particles, which cause fish eye defects)
- stripping temperature and duration (affects color and stability of resin).

Some of these influences (formation of defects) were already discussed and others are discussed in the next chapter.

2.3.4 SOLUTION

If polymer is soluble in solvent, the polymerization reaction proceeds homogeneously. Because of a large chain transfer constant, molecular weight of PVC is also relatively low in solution synthesis. Solution polymerization is not used on a commercial scale because isolation of polymer requires evaporation of solvent, which is not safe and is expensive.

2.3.5 LIVING POLYMERIZATION

Living polymerization of vinyl chloride was patented.[11] The reaction can be initiated by a large number of initiators (for example, mono, di, tri or polyfunctional α,α-dihaloalkane, α,α,α-trihaloalkane, a perhaloalkane, a perfluoroalkyl halide, a polyfluoroalkyl halide, a benzyl halide, an allyl halide, a sulfonyl halide, an α-haloester, an α-halonitrile, an α-haloketone, an imidylhalide, or their combinations) in conjunction with non-metallic reducing single electron transfer reagents as catalysts (salts of dithionous acid, Na_2SO_3, formamidine sulfonic acid, and many others) and accelerated by electron shuttles (1,1'-dialkyl-4,4'-bipyridinium dihalide).[11] The process can be conducted at room temperature in water, producing PVC with a controlled molecular weight and narrow molecular weight distribution.[11]

Single Electron Transfer Degenerative Chain Transfer Living Radical Polymerization (a form of living radical polymerization) permits production of PVC on industrial scale.[12,13] The PVC manufactured by this method has different morphological features which cannot be obtained by conventional free radical polymerization.[12,13]

The above described living polymerization of VC permits production of low molecular weight polymer (M_n=20000) having high thermal stability (frequently better than the currently produced industrial products).[12] It is because much less defects are produced during polymerization and processing.[12]

2.4 POLYMERIZATION CONDITIONS AND PVC PROPERTIES

Polymerization has a profound effect on properties of PVC, including its thermal stability. In order to illustrate these influences, the results of some experimental studies and modelling are discussed below.

Size of reactor influences production output but at the same time increasing reactor size decreases surface area of walls through which reaction mixture can contact the heat exchanging medium. Figure 2.1 shows that the ratio of wall surface to the reactor volume decreases, which means that large reactors are more difficult to cool. Since VC polymerization is an exothermic reaction, a large amount of heat have to be removed in order to keep reaction temperature within process requirements.[6] Reaction temperature can also be controlled by the rate of initiator supply and the initiator properties (half-life temperature). It can be expected that a larger reactor will need to be run at slower rate to balance heat.

The diameter of particles depends on agitation speed (Figure 2.2).[14] There are many other parameters of reaction conditions which influence particle size. Figure 2.3 shows that the energy barrier between two primary particles decreases with particle size increasing.[15] The particle stability is estimated here based on the maximum height of repulsive

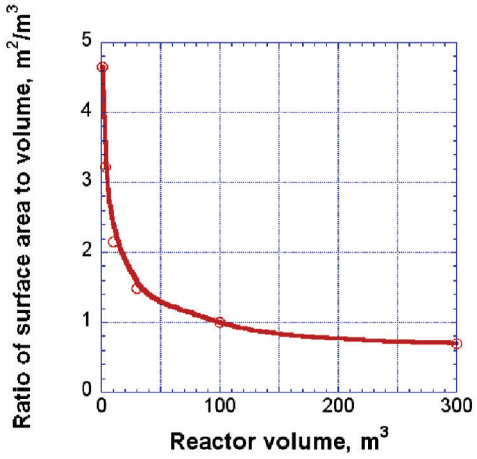


Figure 2.1. Ratio of wall surface area of reactor to its volume. [Data from Saeki, Y.; Emura, T., *Prog. Polym. Sci.*, **27**, 2055-2131, 2002.]

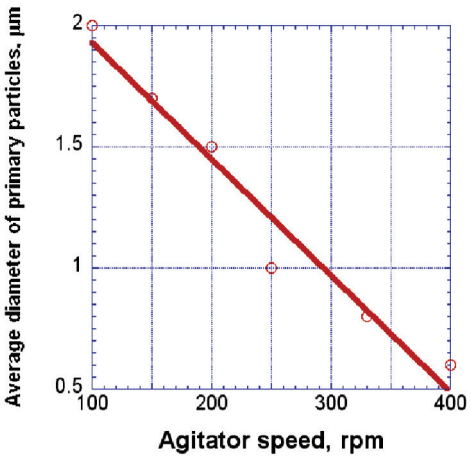


Figure 2.2. Average diameter of PVC primary particles vs. agitator speed. [Data from Zhao, J.-S.; Wang, X.-Q.; Fan, C.-G., *Polymer*, **32**, 14, 2674-2679, 1991.]

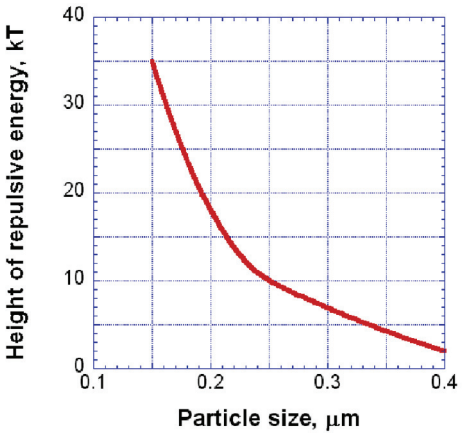


Figure 2.3. Particle stability as maximum height of repulsive energy barrier on particle approach vs. particle size. [Data from Tornell, B.; Uustalu, J. M.; Jonsson, B., *Coll. Polym. Sci.*, **264**, 439-444, 1986.]

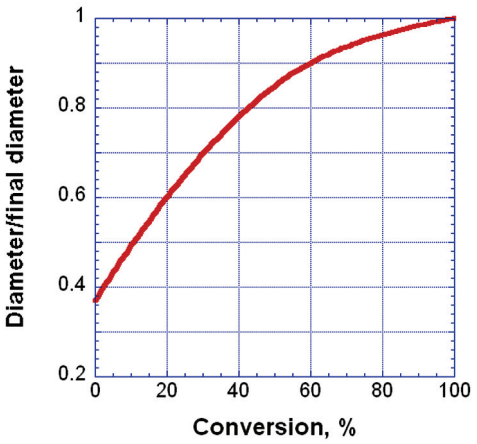


Figure 2.4. Relative mean particle diameter as measured by Coulter counter vs. conversion. [Data from Cebollada, A. F.; Schmidt, M. J.; Farber, J. N.; Capiati, N. J.; Valles, E. M., *J. Appl. Polym. Sci*., **37**, 145-166, 1989.]

energy barrier on particle approach. This shows that larger particles are more likely to coalesce, which underlines the reasons for good mixing.[15]

Initial particles grow further during polymerization because monomer diffuses into primary particles but it is clear from Figure 2.4 that particle size is established very early in the process since further growth changes diameter only by up to approximately 150%.[16] Viscosity of reaction medium is known to contribute to the initial size of particles. Lower

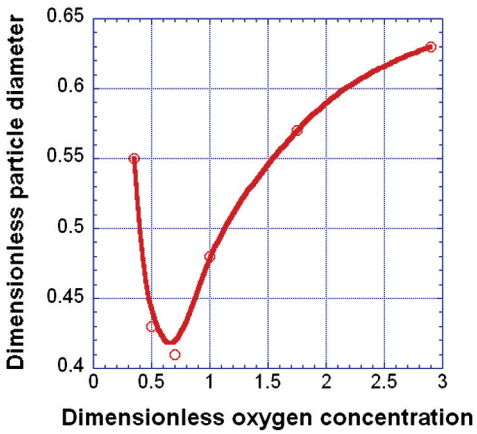


Figure 2.5. Effect of the initial oxygen concentration on the dimensionless average particle diameter. [Data from Kiparissides, C.; Achilias, D. S.; Frantzikinakis, C. E., *Ind. Eng. Chem. Res.*, **41**, 3097-3109, 2002.]

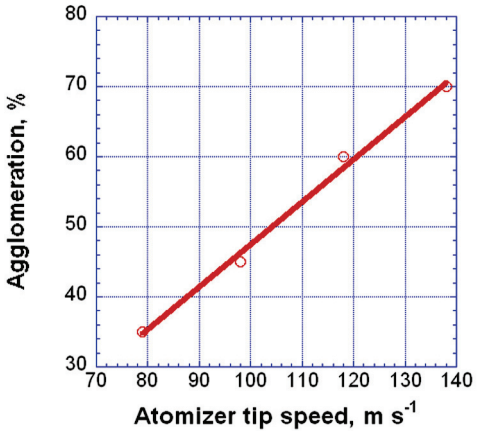


Figure 2.6. PVC agglomeration vs. atomizer tip speed in spray drying of emulsion polymer. [Data from Saeki, Y.; Emura, T., *Prog. Polym. Sci.*, **27**, 2055-2131, 2002.]

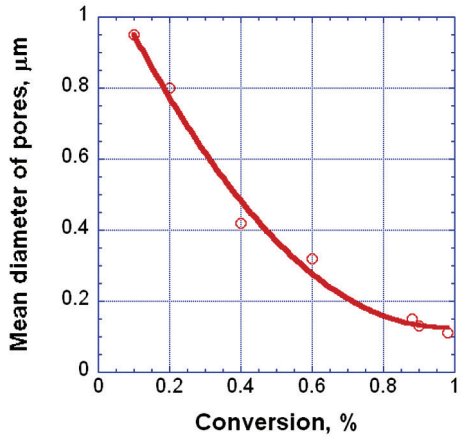


Figure 2.7. Mean pore diameter vs. conversion. [Data from Cebollada, A. F.; Schmidt, M. J.; Farber, J. N.; Capiati, N. J.; Valles, E. M., *J. Appl. Polym. Sci.,* **37**, 145-166, 1989.]

viscosity of reaction medium produces smaller particles.[16]

Oxygen is capable of reacting with initiator primary radicals and oligomers in the aqueous phase to produce vinyl polyperoxides.[17] The vinyl polyperoxides can decompose into radicals, which are capable of initiating new polymer chains. The average particle size exhibited a U-shaped behavior with respect to the initial oxygen concentration. This behavior is explained by the combined role of vinyl polyperoxides as radical generators and ionic strength promoters (Figure 2.5).[17]

Processes following polymerization also affect particle size, as seen from the example of drying emulsion polymerizate (Figure 2.6).[6] Not only atomizer speed but especially inlet and outlet air temperatures affect agglomeration and thus particle sizes. In addition, inlet and outlet temperatures cause initial degradation of PVC.

Pore diameter (Figure 2.7)[16] and porosity (Figure 2.8)[18] of particles decrease with conversion and/or polymerization time increasing. Similar is the case of specific surface area (Figure 2.9), which also decreases with conversion.[14] This is understandable considering that monomer diffuses into polymer grains and fills the available free volume.

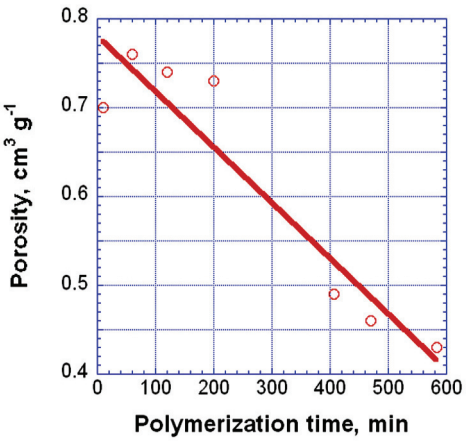


Figure 2.8. Porosity vs. polymerization time. [Data from Scherrenberg, R. L.; Reynaers, H.; Gondard, C.; Booij, M., *J. Polym. Sci., Part B: Polym. Phys*., **32**, 1, 99-109, 1994.]

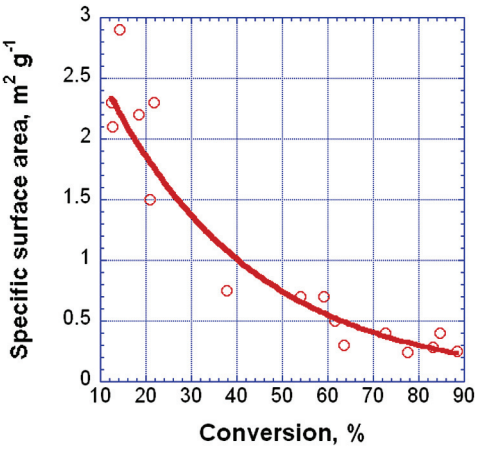


Figure 2.9. Specific surface area of PVC grains vs. conversion. [Data from Zhao, J.-S.; Wang, X.-Q.; Fan, C.-G., *Polymer*, **32**, 14, 2674-2679, 1991.]

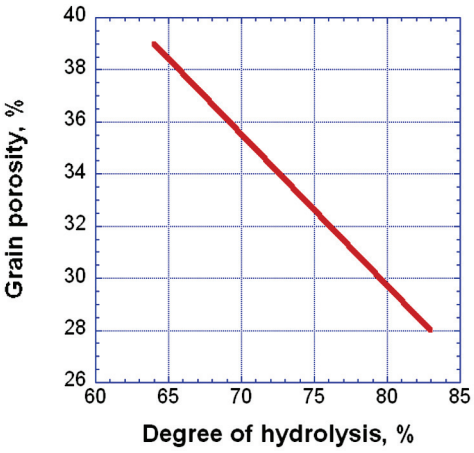


Figure 2.10. Effect of the degree of hydrolysis of PVAc on grain porosity. [Data from Zimmermann, H., *J. Vinyl Additive Technol.*, **2**, 4, 287-294, 1996.]

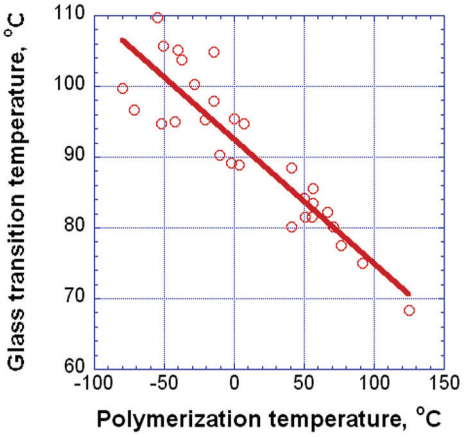


Figure 2.11. Glass transition of PVC vs. its polymerization temperature. [Data from Daniels, C. A., *J. Vinyl Technol.*, **1**, 4, 212-217, 1979.]

Porosity of suspension polymer depends also on composition of reaction mixture. Poly(vinyl alcohol) is frequently used as protective colloid. Poly(vinyl alcohol) is obtained by hydrolysis of poly(vinyl acetate). The degree of hydrolysis, in the range from 45 to 81.5%, affects porosity of PVC particles, as can be seen from Figure 2.10.[2]

Polymerization temperature affects glass transition temperature of polymer which is inversely proportional to polymerization temperature (Figure 2.11).[19] Figure 2.12 shows that glass transition temperature of polymer affects its processing properties.[20] The higher

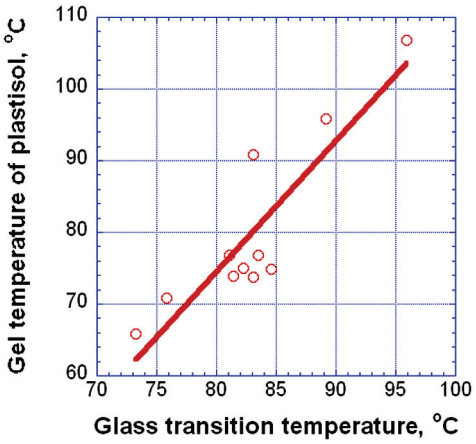


Figure 2.12. Relationship between gel temperature of plastisol and PVC glass transition temperature. [Adapted, by permission from Nakajima, N.; Yavornitzky, C. M.; Roche, E. J.; Harrell, E. R., *J. Appl. Polym. Sci.*, **32**, 1986.]

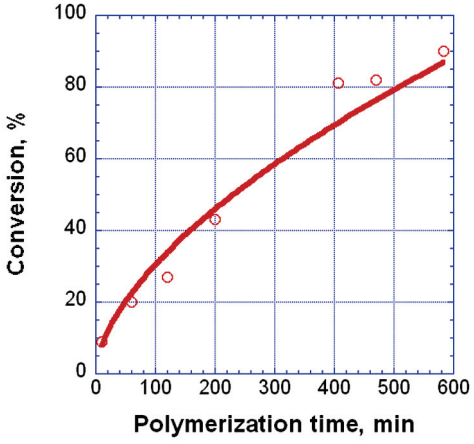


Figure 2.13. Vinyl chloride conversion vs. polymerization time. [Data from Scherrenberg, R. L.; Reynaers, H.; Gondard, C.; Booij, M., *J. Polym. Sci., Part B: Polym. Phys.*, **32**, 1, 99-109, 1994.]

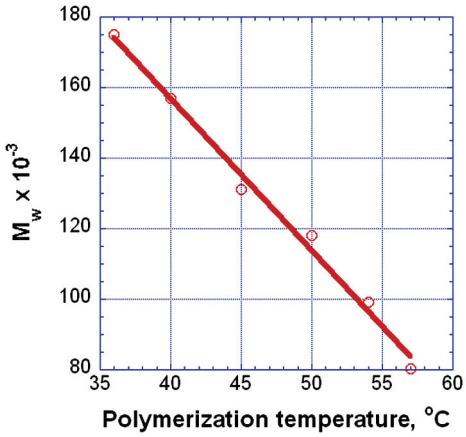


Figure 2.14. PVC molecular weight vs. polymerization time. [Data from Scherrenberg, R. L.; Reynaers, H.; Gondard, C.; Booij, M., *J. Polym. Sci., Part B: Polym. Phys*., **32**, 1, 99-109, 1994.]

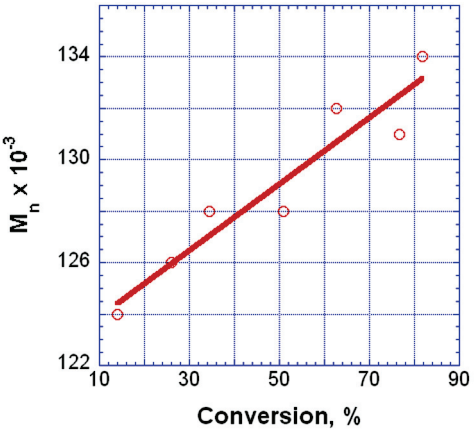


Figure 2.15. PVC M_w vs. monomer conversion. [Data from Bao, Y. Z.; Brooks, B. W., *J. Appl. Polym. Sci.*, **85**, 1544-1552, 2002.]

the glass transition temperature of polymer, the higher the gel temperature of plastisol. Polymers with higher glass transition temperatures require more heat to be processed.

The above influences are not surprising, considering that molecular weight of polymer depends on conversion and polymerization time (Figures 2.13-2.15). Increase in polymerization time under particular conditions increases monomer conversion (Figure 2.13).[18] Increase in polymerization temperatures causes an almost linear decrease in the

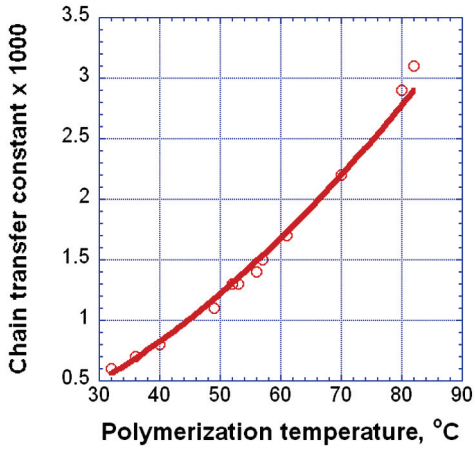


Figure 2.16. Chain transfer constant vs. polymerization temperature. [Data from Starnes, W. H., *Prog. Polym. Sci*., **27**, 2133-2170, 2002.]

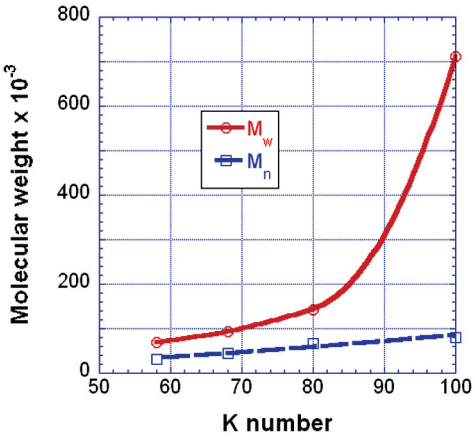


Figure 2.17. The relationship between molecular weight of PVC and its K number. [Data from Rogestedt, M.; Hjertberg, T., *Macromolecules*, **26**, 1, 60-4, 1993.]

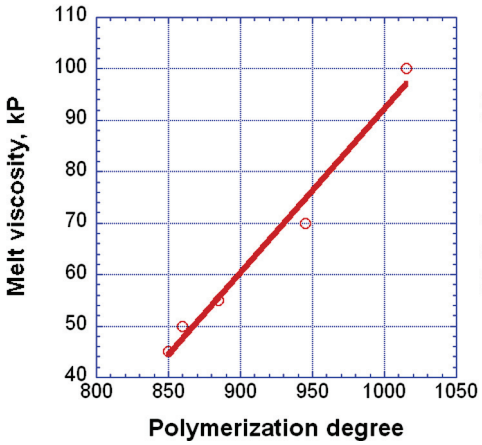


Figure 2.18. Effect of polymerization degree on melt viscosity. [Data from Tripathi, A.; Tripathi, A. K.; Pillai, P. K. C., *J. Mater. Sci.*, **25**, 1947-1951, 1990.]

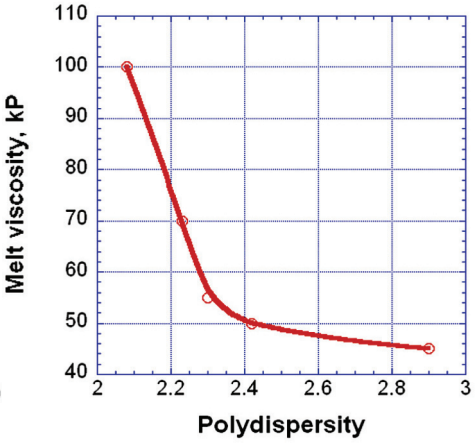


Figure 2.19. Effect of polydispersity on melt viscosity. [Data from Tripathi, A.; Tripathi, A. K.; Pillai, P. K. C., *J. Mater. Sci*., **25**, 1947-1951, 1990.]

molecular weight of PVC (Figure 2.14).[21] Monomer conversion has smaller influence on molecular weight than the polymerization temperature (Figure 2.15).[21] It is so because the chain transfer constant is controlled by polymerization temperature (Figure 2.16).[22] K number correlates with M_n and M_w (Figure 2.17).[23]

Thermal treatment of PVC is related to its polymerization degree and polydispersity. Figures 2.18 and 2.19 show effect of polymerization degree and polydispersity on melt viscosity, respectively. Figures 2.20 and 2.21 show the effect of polymerization degree and

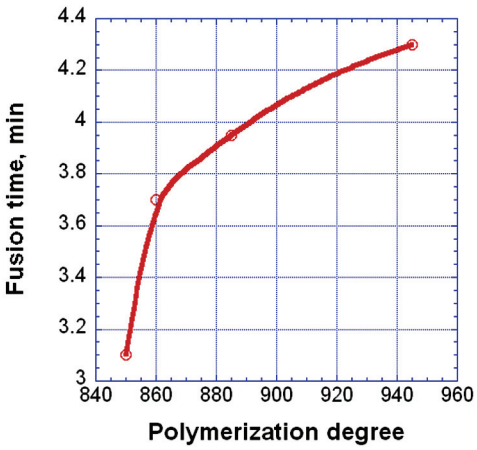


Figure 2.20. Effect of polymerization degree on fusion time. [Data from Tripathi, A.; Tripathi, A. K.; Pillai, P. K. C., *J. Mater. Sci.,* **25**, 1947-1951, 1990.]

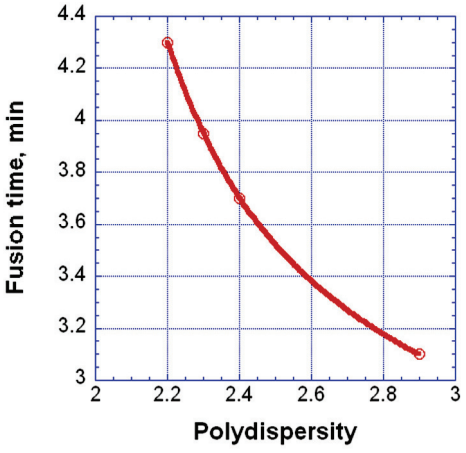


Figure 2.21. Effect of polydispersity on fusion time. [Data from Tripathi, A.; Tripathi, A. K.; Pillai, P. K. C., *J. Mater. Sci.*, **25**, 1947-1951, 1990.]

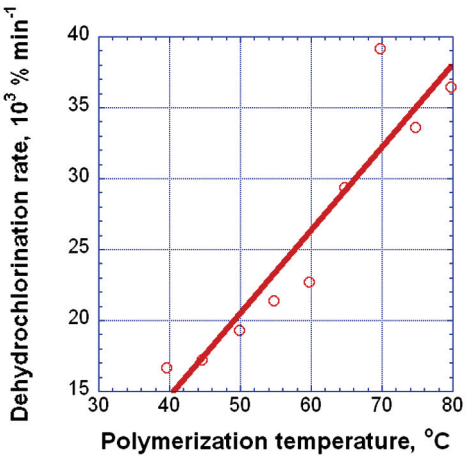


Figure 2.22. Influence of polymerization temperature on dehydrochlorination rate of PVC. [Adapted, by permission, from Xie, T. Y.; Hamielec, A. E.; Wood, P. E.; Woods, D. R.; Chiantore, O., *Polymer*, **32**, 9, 1696-1702, 1991.]

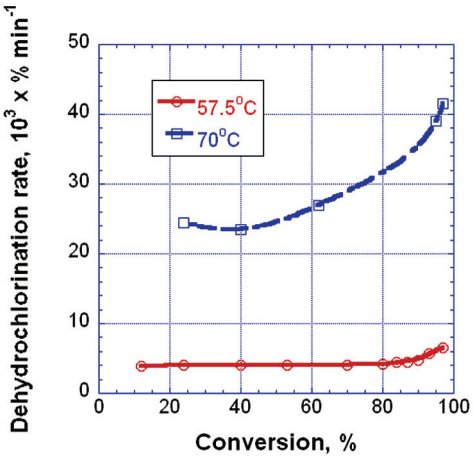


Figure 2.23. Effect of monomer conversion on PVC dehydrochlorination rate. [Data for polymerization at 57.5°C from Purmova, J.; Pauwels, K. F. D.; Van Zoelen, W.; Vorenkamp, E. J.; Schouten, A. J.; Coote, M. L., *Macromolecules*, **38**, 15, 6352-6366, 2005; data for polymerization at 70°C from Xie, T. Y.; Hamielec, A. E.; Rogestedt, M.; Hjertberg, T., *Polymer*, **35**, 7, 1526-34, 1994.]

polydispersity on fusion time, respectively. In both these cases as well as in the case of plastisol the gel time (Figure 2.12), molecular weight and its distribution control the

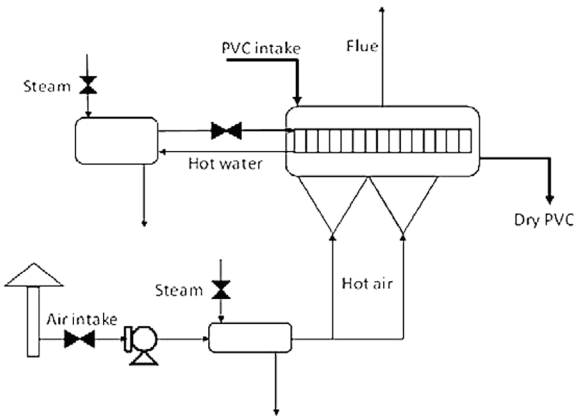


Figure 2.24. Schematic diagram of the continuous PVC fluidized bed drying process. [Adapted, by permission, from de Araujo, A. C B.; Neto, J. J. N.; Shang, H, 10th International Symposium on Process Systems Engineering - PSE2009.

amount of thermal energy required for processing by which they affect thermal stability of polymer.

The direct studies on polymerization temperature and conversion on thermal stability of PVC show that both have a strong effect. Increased polymerization temperature increases dehydrochlorination rate (Figures 2.22 and 2.23). In addition, after initial stages of conversion further polymerization decreases polymer stability (Figure 2.23) because of formation various defects as it was discussed in Chapter 1.

The data which were analyzed in this section show that PVC stability is influenced by conditions of polymerization. These influences together with the structural defects in PVC chain make behavior of PVC dehydrochlorination rate very complex.

2.5 OPTIMAL OPERATION OF INDUSTRIAL PVC DRYER

Several publications are now available on optimal operation of fluidized bed dryer for PVC.[27-29] Figure 2.24 shows a schematic diagram of fluidized bed dryer for PVC.[27] After polymerization, a mixture containing 30% PVC and 70% water is stripped of some water in a centrifuge, the remaining 20-30% water is removed in dryer shown in Figure 2.24. Temperature and outlet relative humidity are controlled in the dryer.[27] Proper control of temperature difference in the dryer allows to save 16% energy required for drying and to increase process output by 22%.[28] Numerical model was developed for control of drying operation.[29] Model further enhances economical operation of the dryer.[29]

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3

PVC Morphology

This is an important subject for understanding the processing behavior of PVC. Unfortunately most monographic sources either omit this discussion or restrict it to a description of PVC grain morphology.

Morphology of a polymer is determined by the size of molecule (molecular weight or molecular weight between crosslinking), structure of chain segments (*cis-trans* isomerization, tacticity, and conformation), chain spatial distribution and interaction (entanglements, spacing, and crystalline structure), and structure of particles (size, primary particles, agglomerates, skins, pores, etc.). This also will be the sequence of our discussion here, which will be finalized by a short discussion on how morphology influences PVC processing, product structure and properties, and its durability.

Few authors have commented on this subject, especially because of the difficulties in either measuring techniques or quantum mechanical calculations. PVC, being a polymer of a low degree of crystallinity, cannot be studied effectively by the usual methods applied to crystalline materials. The major difficulty is in interpretation of results caused by the fact that the morphology is a descriptive feature, not a parameter, because it is influenced by so many variables. In spite of all these difficulties and multidisciplinary character, the available research nevertheless has given us some interesting results, which are commented on below.

3.1 MOLECULAR WEIGHT OF POLYMER (CHAIN LENGTH)

In an ideal case, we would like to have a straightforward correlation between either the molecular weight of polymer or the distribution of molecular weight and its thermal stability and other typical properties of PVC. In the early studies, such research was conducted,[1] resulting in more confusion than clear explanation of the effect of molecular weight on PVC thermal stability. Table 3.1 shows some of the data.[1]

Table 3.1. The number-average molecular weight versus PVC dehydrochlorination rate. [Data from Crosato-Arlandi, A.; G. Palma, G.; Peggion, E.; Talamini, G., *J. Appl. Polym. Sci*., **8**, 747, 1964.]

M_n	**Polymerization temp.**, K	**Dehydrochlorination rate**, 10^6 dx/dt, s^{-1}
55,000	298	1.66
95,000	273	1.78
142,000	253	1.56
136,000	233	1.61

Table 3.1. The number-average molecular weight versus PVC dehydrochlorination rate. [Data from Crosato-Arlandi, A.; G. Palma, G.; Peggion, E.; Talamini, G., *J. Appl. Polym. Sci*., **8**, 747, 1964.]

M_n	**Polymerization temp.**, K	**Dehydrochlorination rate**, 10^6 dx/dt, s^{-1}
93,000	213	2.33
79,000	195	1.87

If molecular weight is mainly controlled by transfer reactions (only a small amount of polymer is produced by termination), the molecular weight and branching development can be calculated as follows: [2,3]

$$dQ_0/dX = C_M$$

$$dQ_1/dX = 1$$

$$dQ_2/dX = 2\frac{1 + C_pQ_2}{C_M + C_pX/(1-X)}$$

$$\frac{d(Q_0\overline{B}_n)}{dX} = C_p\{X/(1-X)\}$$

$$C_m = k_{fm}/k_p = C_{M0}\exp\left\{B_m\left(\frac{1}{V_F} - \frac{1}{V_{FcrM}}\right)\right\}$$

$$C_p = k_{fp}/k_p = C_{p0}\exp\left\{\frac{1}{V_F} - \frac{1}{V_{Fcrp}}\right\}$$

$$\overline{M}_n = M_mQ_1/Q_0 = 62.5X/Q_0$$

$$\overline{M}_w = M_mQ_2/(Q-1) = 62.5Q_2/X$$

$$\bar{\lambda}_n = 1000M_R(B_n/M_n)$$

where:

- X monomer conversion,
- B_n number-average of branch points per polymer molecule, n
- k_{fm} transfer-to-monomer rate constant,
- k_p propagation rate constant,
- k_{fp} transfer rate constant,
- M_n number-average molecular weight of polymer,
- $\overline{M}_w$ weight average molecular weight of polymer,
- V_F transfer rate,
- $\bar{\lambda}_n$ number of long branches per 1000 monomer units,
- M_R molecular weight of the repeat unit,
- B_m, B_p, V_{FcrM}, V_{Fcrp} parameters which can be found by fitting the rate and the molecular weight data.

From the above model and data derived from calculations,[2] the number of long branches is inversely proportional to the polymer molecular weight. The molecular weight of commercial polymers manufactured in the 1980s, expressed by $\overline{M}_n$, varied in the range of 35,000 to 80,000 (Fikentscher K value 60 to 95), and only in the beginning of the 1980s, due to the improvements in the polymerization process, the lower limit was decreased from 45,000 to 35,000, which was not possible for a long time. In the 1990s, most commercial polymers were produced in the same range of molecular weight as experimentally confirmed by Pang and Rudin.[4]

In the 21st century, typical molecular weight of commercial polymers was found to be in the range given in Table 3.2.

Table 3.2. Range of molecular weight of commercial polymers. [Data from refs. 5 and 6]

Polymer type	K	M_n
Suspension	50-95	20,000-70,000
Mass	58-69	26,000-38,000
Emulsion	60-80	29,000-50,000

Data in Table 3.2 show that molecular weight of commercial polymers shifted to lower values than in the previous century. This is a result of perfected technology of manufacturing as well as demand for resins which can be processed faster and with less energy.

Polydispersity of commercial polymers in the 1990s was found to be in the range of 2.2 to 5.8.[4] The recently produced commercial resins have a very narrow range of polydispersities (suspension – 1.9 to 2.6, emulsion – 2.1 to 2.6, and mass – 2.0 to 2.1).[5,6]

There are two concepts related to the molecular weight: mean molecular weight between crosslinks and molecular weight between entanglements. The mean molecular weight between crosslinks can be determined from the swelling rate of polymer preimmersed in tetrahydrofuran.[7] The mean molecular weight between crosslinks is calculated from the following equation:

$$\overline{M}_c = \frac{V_1 \rho_2 (v_2/2 - v_2^{1/3})}{\ln(1 - v_2) + v_2 + \chi_1 v_2^2} \qquad [3.1]$$

where:

V_1 molar volume of tetrahydrofuran (76.33 ml mol^{-1})
ρ_2 PVC density
v_2 PVC volume fraction
χ_1 the interaction parameter of the PVC-THF system.

The critical end-to-end distance of a macromolecular chain for entanglements corresponds to the critical molecular weight of entanglement, M_c.[8] The critical end-to-end distance is calculated from critical molecular weight of entanglement, M_c, using the following relationship:[8]

$$\langle R_c \rangle = M_c^{1/2} \{ \langle R^2 \rangle_0 / M \}^{1/2} \qquad [3.2]$$

where:

$\langle R_c \rangle$	critical end-to-end distance for entanglements
$M_{c\,2}$	critical molecular weight
$\langle R^2 \rangle_0$	mean-square end-to-end distance for polymer
M	molecular weight of polymer.

The studies of entanglements compared end-to-end distance for entanglements with chain diameter for many polymers. The chain diameter can be obtained from the following equation:[8]

$$D = S^{1/2} \qquad [3.3]$$

where:

S cross-sectional area of polymer obtained from crystallographic data.

Critical end-to-end distance increases with increasing molecular diameter. Thicker chains form longer entanglements, most likely because rigidity of chain increases with molecular diameter. Out of 36 polymers tested, PVC has relatively short M_c (6,250; M_c for tested polymers varies from 2,500 to 114,000; and relatively small chain diameter of 0.52 nm; chain diameters for the tested polymers ranged from 0.42 to 11.6 nm).[8]

Chapter 1 characterizes changes in the composition and structure of PVC at different rates of conversion and molecular weights. In the beginning of this chapter, an example is given (Table 3.1) which shows that molecular weight is not the only parameter controlling its thermal stability. From Chapter 1 it is known that polymerization conditions affect concentration of labile groups. The effect of these groups on PVC thermal stability will be discussed in depth in Chapter 4.

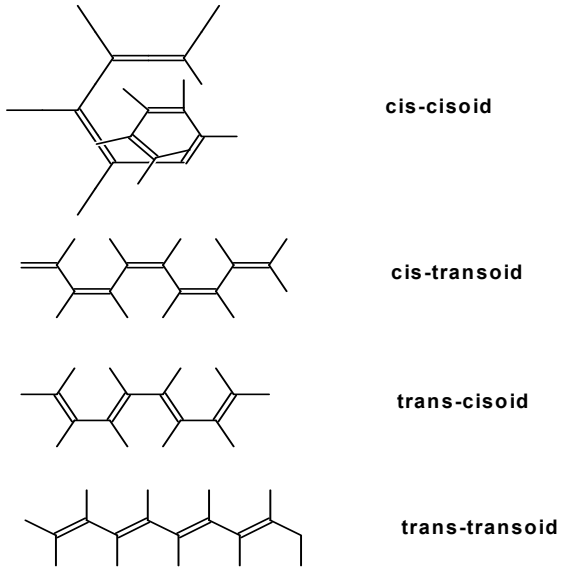
Many other processing results and parameters are affected by molecular weight and its distribution. Figures 2.18 and 2.19 show that melt viscosity is affected by molecular weight and its distribution. Figures 2.20 and 2.21 show the effect of molecular weight and its distribution on fusion time. Gelation of plastisols[9] and sheets manufactured by roll milling[10] was also enhanced by lower molecular weight PVC.

In industrial practice, a technological compromise is the most usual case. Impact resistance, weather stability, and cost were the factors analyzed to develop the process of production of extruded PVC profiles.[11] Impact modification was thought to be affected by the type and the concentration of impact modifier and the molecular weight of PVC resin. Cost was mostly determined by the production rate and the amount of impact modifier. Production rate can be optimized by reducing molecular weight of resin but reduction of molecular weight causes decrease in impact strength. These two effects impact the choice of PVC resin to favor medium molecular weight. With such resin it is possible to maintain required impact strength and produce profiles with increased rate and low concentration of impact modifier.

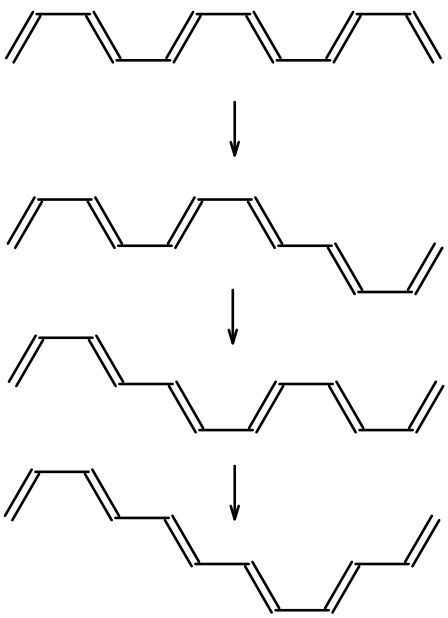
3.2 CONFIGURATION AND CONFORMATION

The first-order structure of the polymer chain is determined by mers arrangement, configuration and conformation. The mers arrangement includes head-to-head and head-to-tail structures that have already been discussed. By configuration one should understand the spatial arrangement of atoms, and groups formed by them, in reference to a particular point of a chain-like center of asymmetry or chain backbone. Structural isomerism is the simplest form of configuration. All structural isomers have the same number of atoms (the same empirical formula) but physical properties of isomers are different. Hydrocarbon having 30 atoms may theoretically form 4,111,846,763 isomers. Polymers have a much larger number of monomeric units, therefore, potentially, they may form an infinite number of structural isomers. In practice, the amount of these isomers is restricted by a mechanism of polymerization which favors a preferred arrangement, but still a polymer is a mixture of a large number of structural isomers. Chain branching is one of the resultant structures of structural isomerism. This subject was extensively investigated in Chapter 1 and implications of structural isomerism on PVC degradation are discussed in the next six chapters in reference to their influence on thermal, UV, irradiance, high energy, mechanical, and chemical degradations.

Geometrical isomerism is another subset (or type) of configuration. It occurs when double bonds are present in a molecule. It is popularly known as *cis-trans* isomerism. *Cis-trans* isomerism has not been studied in PVC, either experimentally or by molecular calculations; therefore, in order to explain this phenomenon, we may search data for related substances. We have two possibilities: either to consider the low molecular models having a similar number of conjugated double bonds, such as, for example, carotenoids (but in this case we shall expect the influence of an ionon ring on charge distribution and on conformational changes); or we may consider a polymer having in its backbone a conjugated double bonds, and here polyacetylene serves as a good example. Based on the results of polyacetylene studies,[12-20] we are able to say more about the polyene structure. Polyacetylene exists in four configurational forms that are well characterized by the following structures:



If the polymer is obtained at considerably low temperature (e.g., 195K), it yields primarily *cis*-$(CH)_x$, which is, however, a thermodynamically unstable form that is subsequently isomerized into all-*trans* polyacetylene. The polymer initially obtained by low temperature polymerization exists in the *cis-transoid* conformation. The isomerization process can occur due to thermal treatment, even at low temperatures; for example, it was discovered that isomerization occurs during IR spectrum measurement, at which the temperature was estimated to be around 313K. The activation energy of the isomerization process is initially very low (67 kJ/mol). As the isomerization process continues, the activation energy increases to 117 kJ/mol. It is thought that the first step in isomerization is defect-induced.[18] Considering structural changes, gradual isomerization occurs by rotation around single bonds as shown below:



It continues until an all-*trans* structure is finally obtained. The isomerization process is temperature controlled, and full conversion takes place at 453K in just a few minutes. The changes which take place are irreversible; the trend always observed is from *cis* to *trans* and never the opposite.

It is interesting to notice that there is a difference in color between both *cis* and *trans* forms. While the *cis* form is blue, the *trans* form is red. It is therefore evident that what we observe in PVC is evidently the *trans*-form.

Now, we should realize what this type of configuration means in the case of PVC. When the initial PVC lacks a conjugated system, its conformation (previously discussed) is either helical or lamellar – in other words, the polymer has developed a spatial arrangement and great freedom to change it. If during degradation we expect the formation of *cis-transoidal* or *trans-cisoidal* forms, the situation would not be changed much, since they also have both the freedom to change conformation and a three-dimensional spatial arrangement. But if, due to isomerism, we arrive at an all-*trans* form, this part of the polymer has a flat, rigid conformation, so the degraded polymer has a certain rigidity contributed by the degraded sequences. This has serious implications in technology. In PVC products the thermal treatment affects the elasticity of material.

Studies on polyacetylenes should help us in understanding some phenomena which were not revealed for PVC, and at the same time, this knowledge may stimulate an interest in PVC studies which may shade more light on its structure. We will now compare the above discussed findings with observations known from PVC studies.

Tran *et al*.[21-25] developed polaron theory to explain thermal dehydrochlorination of PVC. Polarons are a result of oxidation of conjugated systems formed during dehydrochlorination and subsequent isomerization. The polaron theory will be discussed in detail in the next chapter. Chatterjee[26] put forward the mechanism of degradation occurring during thermal analysis. According to his theory, the structural reorganization (*cis-trans* isomerization) is one of the stages of degradation process.

Fisch and Bacaloglu[27,28] studied *trans*-6(4)-chloro-4(5)-tetradecene as a model compound of PVC dehydrochlorination. They found that a mixture of *trans-trans* and *trans-cis*-tetradecadienes is formed on heating. *Cis*-6(4)-chloro-4(5)-tetradecenes are formed as intermediates. Based on this observation they suggested that the HCl loss takes place *via* 1,4-elimination through a six center transition state from a *cis*-allylic chloride.

Energy calculations by Karpfen and Hoeller[29] have shown that *trans-transoid* is the most thermodynamically stable structure in PVC – the same as in polyacetylene. It is now well-known and documented that PVC can degrade thermally, photochemically, and chemically by elimination of HCl and formation of all-*trans* polyenes.[30,31] Short polyenes are produced photochemically, mainly in the *cis*-form, which is generally thermally unstable and it is converted, at 65°C, into more stable *trans* isomer.[32]

For the Diels-Alder reaction to occur, the diene must be in the *cisoid* conformation, whereas the expected preferred conformation of polyene sequences in partially dehydrochlorinated PVC is *trans*.[33] Although there is conclusive evidence that Diels-Alder adducts are formed between partially dehydrochlorinated PVC and some maleate esters, this reaction does not prevent formation of long polyene sequences. It was therefore postulated[33] that the steric hindrance of interconversion from *trans* to *cis* form considerably slows down the progress of Diels-Alder reaction, making it not useful in stabilization.

Pinking can be observed in PVC window and door profiles exposed to the mild environmental conditions of northern European countries. The pinking phenomenon is caused by formation of polyene sequences, which are not completely photooxidatively bleached. The fast phototransformations in visible light of chloropolyenes in *trans*-configurations leading to α-chloropolyenes in *cis*-configurations account for the conversion of pinking into limited graying which occurs in the presence of lead stabilizers.[34]

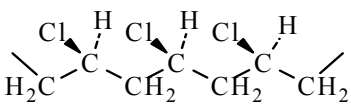
It is obvious from the above conclusions of studies on PVC that PVC behavior can only be fully understood if geometrical isomerism is taken into consideration in development of mechanisms of PVC degradation and stabilization.

Stereoisomerism occurs as a result of the presence of a three-dimensional structure in certain polymers. An important requirement that all four substituents to carbon atom are different is fulfilled by PVC. The carbon atom which has four different atoms or groups attached is called an asymmetric carbon atom. The asymmetric carbon atom may exist in two different forms which are mirror images of each other. Stereoisomerism essential for some polymers including PVC is better known as a tacticity. Comparing optical isomerism with tacticity, one should mention that, while physical properties of optical isomers are the same (except for light polarization), polymer tacticity affects physical and mechanical properties of polymer such as strength and elasticity, light absorption, phase transition temperature, crystallinity and many other properties.

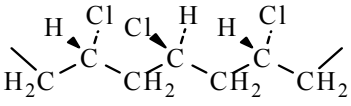
Polymer tacticity exhibits three basic structures:

- isotactic, in which all the groups are on the same side of a chain (in PVC, all the Cl atoms);
- atactic, in which these groups are randomly and irregularly distributed;
- syndiotactic, in which groups, e.g., Cl, are regularly distributed on both sides of the chain or its segment in alternative arrangement.

Isotactic and syndiotactic segments can be expressed by the following structures:



isotactic



syndiotactic

Configurational content can be studied by high resolution NMR, IR and Raman spectroscopies. NMR spectroscopy was used by Sorvik[35] who distinguished six bands assigned to syndio-, iso-tactic and combined sequences. The chief drawback of this method is that it can be used only for polymers in solution, while highly syndiotactic polymers are insoluble; moreover, they may change their initial properties in solution and under conditions of dissolution.

IR spectroscopy is the most frequently applied method for tacticity evaluation. In this method, by comparing the intensities of two bands, one can obtain an index of tacticity. Most frequently used ratios are A615/A690[36] and A1428/A1434.[37] The sample preparation method plays an important role here, as can be seen from data in Table 3.3.

There is an evident correlation between both sets of data, but the values differ considerably. From this and other studies,[38] it is evident that the tacticity index increases when polymerization temperature decreases. Martinez[39] determined the PVC dehydrochlorination rate for samples of varying tacticity index obtained by fractionation of polymers of varying polymerization temperature. Figure 3.1 shows the relationship of both values.

Table 3.3. Tacticity index measured by IR in KBr pellets and cast film. (Data from Ref. 36.)

Polymerization temperature, K	Tacticity index	
	KBr disc	cast film
318	1. 25	1. 75
258	1. 50	2.20
233	1. 62	2.40
213	1. 60	2.55
183	2.28	3.30

Martinez[39] explains the increase of dehydrochlorination rate, which is parallel to the increase in syndiotacticity, by easier propagation of polyenes along syndiotactic sequences as compared with their propagation along atactic sequences. His explanation is based on

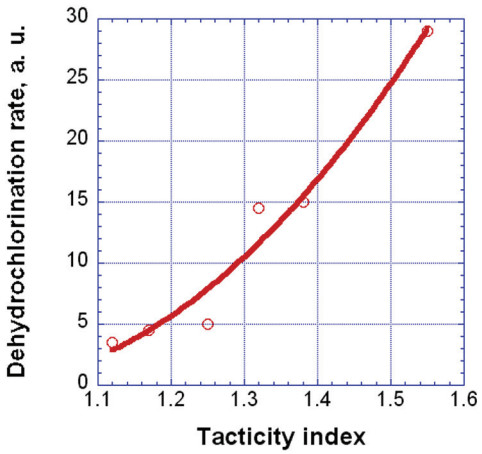


Figure 3.1. PVC dehydrochlorination rate at 453K up to 0.3% conversion vs. tacticity index of polymer. [Data from Martinez, G.; Millan, J., *J. Macromol. Sci.-Chem.*, **A12**, 489, 1978.]

studies of chain scissions (by ozonolysis) for samples degraded to 0.1 and 0.3% conversion. The difference in the number of chain scissions for a sample with the lowest tacticity index (1.2) is very high, while there is no considerable change in the number of chain scissions for two other samples of tacticity index 1.5 and 1.62. Unfortunately, the data as presented cannot be used to estimate if initiation can be correlated with tacticity index because the authors[39] did not give the number of scissions for virgin polymer. Instead, they compared only the molecular weight of initial polymer with the molecular weight of polymer which was degraded and then subjected to ozonolysis. Therefore, the final result includes the sum of double bonds initially present in the polymer and those newly formed. In further studies by the same research group,[40] we can find data showing that the initiation begins more easily from atactic sites than it does at syndiotactic ones. In summary, the syndiotactic segments are less vulnerable to degradation initiation but they promote polyene propagation after it begins. More recent studies[41] show that the tacticity of macromolecules has no significant influence on the initial stage of the thermal degradation of PVC (or its initiation). This subject will be further discussed below as a part of analysis of the effect of conformation on various aspects of PVC behavior.

Polymer tacticity influences other properties of polymer. It has a major influence on crystallinity. Isotactic and syndiotactic fragments can become crystalline, but the atactic ones are usually completely amorphous.[42] The crystallinity occurs due to the folding and entanglements of the long molecular chains with bulky side groups. The bulkier and longer the side groups, the more the entanglements and folds, the higher the crystallinity. Through crystallinity, tacticity affects many other properties of PVC as discussed in a separate section of this chapter.

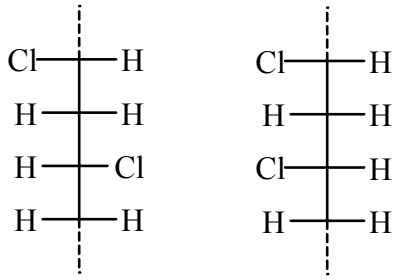
The tacticity has a significant influence on the microstructure caused by steric hindrance. Isotacticity induces a TGTG conformation (G and T refer to "gauche" and "trans" conformations of chain). This is responsible for a helical shape of the chain. Syndiotacticity induces a TTTT conformation which gives an origin to a "zigzag" shape of the chain More explanation on the subject of conformation follows).[43] Syndiotactic segments bring chains closer together due to increased hydrogen bonding. Thus, syndiotacticity lowers free volume and mobility of chain more extensively than isotacticity.

It is suggested that tacticity causes antiplasticization. Antiplasticization causes an increase in modulus and in tensile strength and a progressive disappearance of β-transition which is opposite to the expected action of plasticizer.[44] According to morphological stud-

ies the antiplasticization originates from the occurrence of strong and specific interactions between structures associated with long isotactic sequences and the plasticizer, thereby hindering the motions at the latter structures.[44]

The last two cases base their conclusions on studies of PVC conformation. So far, discussed configuration refers to the order that is determined by chemical bonds. The configuration of a polymer cannot be altered unless chemical bonds are broken and reformed. Conformation refers to the order that arises from the rotation of molecules about the single bonds. Conformation is thus a spatial arrangement of substituent groups that are free to assume different positions in space without breaking any bonds, because of the freedom of bond rotation.

Several typical notations are used to describe conformation of polymer chain. Two adjacent structural units form a diad. Meso diad consists of two identically oriented units, and racemo diad of two opposite oriented units:



racemic r trans T syndio- **meso m gauche G iso-tactic**

Synonyms and their notations are given below Fischer projections showing structures of these diads. Triads contain three adjacent structural units. Isotactic triad has notation mm or GG and syndiotactic triad has notation rr or TT. Longer microconformers are tetrads, pentads, etc. Thermodynamical stability of macroconformer depends on its structure. The more stable the conformer, the lower Gibbs' free energy. Isotactic and syndiotactic conformers have the lowest Gibbs' free energy and that is why they are thermodynamically most stable. At the same time, each conformer has freedom of assuming different position without breaking any bonds under influence of thermal energy by rotating around single bonds.

Figure 3.2 shows that with increasing concentration of syndiotactic triads, the stability of PVC increases. The concentration of isotactic triads decreases with increasing concentration of syndiotactic triads.[45] This figure shows one fundamental observation from conformation studies which, with some exceptions,[41] is the generally accepted common view.

The activation energy for isotactic addition is higher than that for syndiotactic addition by approximately 500–600 cal/mol. Thus, the content of syndiotacticity of the PVC obtained from radical polymerization decreases with increasing reaction temperature.[46]

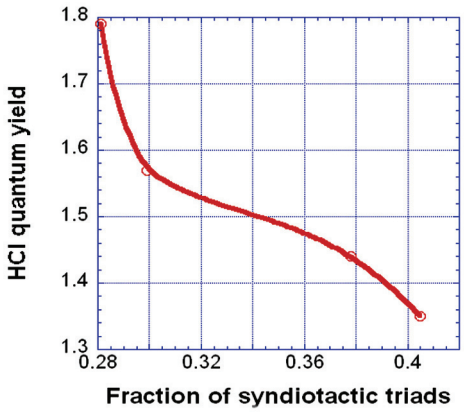


Figure 3.2. Fraction of syndiotactic triads vs. quantum yield of dehydrochlorination. [Data from Castillo, F.; Martinez, G.; Sastre, R.; Millan, J.; Bellenger, V.; Gupta, B. D.; Verdu, J., *Polym. Deg. Stab*., **27**, 1-11, 1990.]

It was observed[47] experimentally that syndiotactic sequences give rise to longer polyenes. MINDO calculations give the following explanation of these findings.[48] After the initial C=C bond is formed in the syndiotactic TTTT triads, polyene growth proceeds quickly because the dihedral angle between the C=C bond and the atoms being eliminated is favorable for allyl activation. In the isotactic TGTG triads, the C=C bond is deviated from the plane of the transition state which causes increase in the activation energy with consequent deceleration of the growth of polyene sequences.[48] Similar observations regard UV degradation of PVC.[49] If degradation is conducted below T_g, longer polyene sequences are formed because the original syndiotactic sequences are better retained at lower temperatures.

3.3 CHAIN FOLDS

Chain folds should be discussed together with other data concerning the crystalline structure of PVC, as they are part of the same phenomenon. An exception was made because the results discussed here are based on potential-energy calculations contrary to the experimental nature of data that is included in crystalline-state studies discussed below in this chapter. The data presented on chain folds are based on the only available publication so far.[50] Some of the input data on which calculations are based include X-ray measurement results of syndiotactic PVC obtained from 0.1% solution in chlorobenzene cooled from 423K.[51] The bond length and angles are assumed for the usually used values for PVC. The model is composed of two stems, each one formed from 18 vinyl chloride monomer units joined by a fold. The resulting models corresponding to (010) and (400) folds are shown in Fig. 3.3.

It is interesting that good contact among atoms of different stems is lacking, which is caused by the length that fold can assume in its allowed conformation. Weak C–H...Cl–C hydrogen bonds are present in the fold region. The presence of such bonds was predicted earlier from IR studies in which presence of a 64 cm^{-1} band was recorded.[52] The other interesting feature of these folds is connected with their rather inflexible nature, which opposes the closer approach of the stems. When investigators introduced one ethylene monomer into the fold, they obtained better crystal packing, due to fold flexibility.

These studies, although based on an assumption which cannot be easily confirmed experimentally, seem to suggest other possibilities when considering the PVC thermal degradation process. Earlier it was said that syndiotactic configuration diminishes the probability of initiation, which might eventually be explained by the chain rigidity observed in these studies. The proposed lack of chain flexibility and its uniform structure,

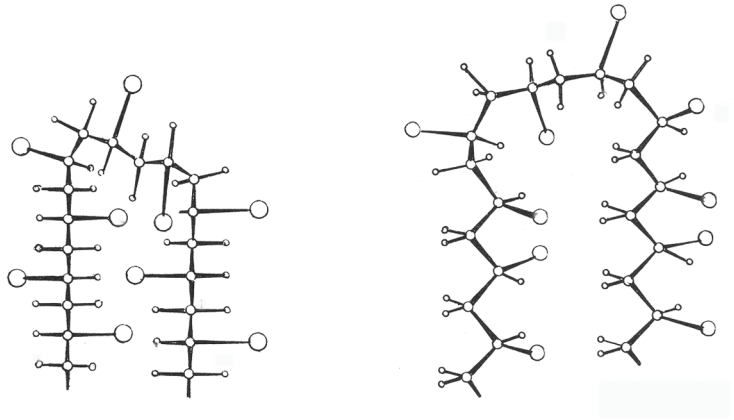


Figure 3.3. (010) and (400) folds of syndiotactic PVC. [Adapted, by permission, from Conte, C.; D'Ilario, L.; Pavel, N. V.; Giglio, E., *J. Polym. Sci., Polym. Phys. Ed*., **17**, 753, 1979.]

if confirmed, should have important implications on the model of degradation. It is true that the energy needed for folding and refolding is always available during the degradation process, but at the same time the possible presence of ordered structures would always decrease the reaction probability and should contribute to better system stability. Observations from these studies could be relevant for an explanation of the contradictory facts mentioned by Braun in his review article.[53] Commenting on studies on the effect of syndiotacticity on PVC thermal stability, Braun observed that from one perspective it is proven that higher syndiotacticity increases the dehydrochlorination rate as confirmed by Milan's results, but at the same time it is known that polymer obtained at lower temperatures (more syndiotactic) is also more stable. Braun explained this contradiction in both trends by the possible influence of other factors, such as various labile structures, molecular weight and so on. Actually, Milan pointed out that only polyene propagation is faster with syndiotacticity increase, while the initiation rate is lower. These two features are regulated by different principles. In the case of propagation, the energy level plays an essential role. It is regulated by the overall charge distribution related to chemical structure and configuration as well, without reference to HCl and other catalytic effects. On the other hand, initiation probability is related (among other factors) to collision probability, which should be lower when part of the chain is in a restricted configuration state.

Summarizing the above, it is difficult to say at the moment how far these structural properties determine the degradation mechanism, since the information available is too limited, but it is important to consider the existence of structural factors, as they may prove relevant in explaining certain phenomena. More recent literature does not discuss these studies.

3.4 CHAIN THICKNESS

Privalko,[54] based on the following equation:

$$A = v_C M / dN_A = m_0 v_C / d_0 N_A \quad [3.4]$$

where:

A		macromolecular cross-sectional area ($A = a^2$),
a		chain thickness,
v_C		crystalline specific volume,
M		molecular weight of monomer unit,
d		identity period,
m_0	=	M/n,
n		number of main chain bonds in mer,
d_0	=	d/n,
N_A		Avogadro's number.

has calculated chain cross-sectional areas for different polymers. For vinyl polymers this equation can be simplified as follows:

$$A = 1.41 m_0 \quad [3.5]$$

From these calculations, we have a value for PVC of 2.718 nm, and for polyacetylene, 1.828 nm. These values may not correspond to values obtained from either crystallographic measurement or conformational calculations. From conformational calculations Conte[51] has arrived at a lamellar thickness of 6.0 nm for PVC which seems to be in the range of the above thickness. From the small angle diffraction, the X-ray long spacing for PVC also equals 6.16 nm.[55] For *cis*-polyacetylenes the lamellar thickness is estimated to be in the range of 5-10 nm, while for all-*trans* conformation it should be as estimated by Privalko.[54]

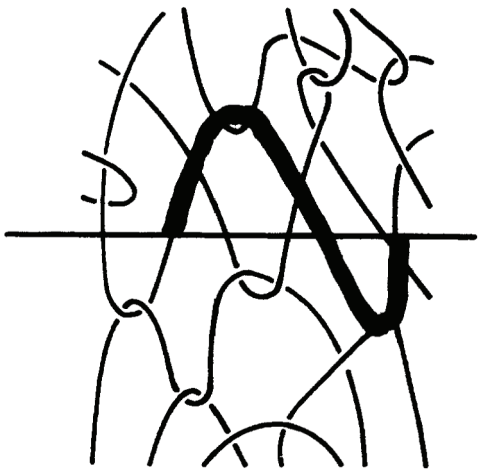


Figure 3.4. Entanglements in polymer melt. [Adapted by permission, from Wool, R. P., *Macromolecules*, **26**, 7, 1564-9, 1993.]

3.5 ENTANGLEMENTS

Entanglements result from the interpenetration of random-coil chains and are important in prediction of synthesis of PVC, its rheology, fusion, crazing, UV and thermal stability, shape memory, and fracture properties.

Figure 3.4 shows an entangled linear chain network. An entanglement network in an isotropic concentrated melt can be explored by counting the number of bridges and chains intersecting an arbitrary plane, as shown in Figure 3.4. A bridge is a segment of chain which crosses the plane three times (bold section of chain in Figure 3.4). It is sufficiently long to complete one circular loop through the plane. The bridge is

capable of transmitting forces across the plane in the melt for a time dependent on the relaxation of this chain segment.[56] The number of chain segment crossings per unit area is independent of molecular weight, but the number of chains intersecting the plane decreases with increasing molecular weight. Thus, by varying the molecular weight, we can reach a state where the number of bridges is comparable to the number of chains.

The number of bridges per chain is given by the following equation:[56]

$$p_c = \frac{1}{2}\left(\frac{p}{n} - 1\right) \qquad [3.6]$$

where:

p_c number of bridges,
p number of chain segment crossing per unit area,
n number of chains intersecting the plane.

Critical molecular weight of entanglement is given by the following equation for vinyl polymers:[56]

$$M_c \approx 30 C_\infty M_0 \qquad [3.7]$$

where:

M_c critical entanglement molecular weight,
C_∞ = characteristic ratio,
M_0 monomer molecular weight.

Critical molecular weight of an entanglement determined experimentally for PVC was 11,000 which compares with 10,700 obtained from modelling.[56]

There is still another parameter used to quantify length of entanglements. It is the critical end-to-end distance for entanglements given by the following equation:[57]

$$R_c = M_c^{1/2}(\langle R^2\rangle_0 / M)^{1/2} \qquad [3.8]$$

where:

$\langle R\rangle_0$ the mean-square end-to-end distance for polymer having molecular weight M in the *theta* solvent

Using this equation we can calculate critical end-to-end distance for PVC to be 8.4 nm and chain thickness of 0.52 nm.

During polymerization, at high conversions, monomer concentration decreases with conversion, the number of chain entanglement points increases rapidly and the bimolecular-termination rate constant for polymer radicals falls dramatically.[58] This causes formation of an increased number of short and long branches and thus structural defects which increase degradation of PVC. More numerous long branches give greater probability of chain entanglement during processing.[59]

UV degradation rate is also affected by changes in entanglements. When, in the course of degradation process, the molecular weight becomes lower than a critical value M_c, the entanglement network is destroyed, plastic deformation cannot occur and the

toughness decreases sharply by two or three orders of magnitude.[60] Cracks propagate rapidly in the oxidized layer and material is considered severely degraded.

The degree of polymer fusion strongly affects entanglements.[61] An increase in the degree of fusion causes a higher density of entanglements and secondary crystalline junctions. Fusion is a function of temperature, shear, and time. A proper fusion level is necessary for good mechanical properties. The fusion process involves melting and reforming of crystallites and molecular entanglement by diffusion.[62] Increased entanglements during processing also apply to polymeric additives such as process aids.[63] These entanglements with process aids strongly increase the mechanical properties of PVC. Higher elongation at break, higher elasticity, and higher melt strength result from increased entanglements with process aid.[63]

Polymers having a high chain entanglement density tend to deform by shear yielding (polycarbonate, polyamide, polyester, polyethylene, and polypropylene are examples). Polymers having a low chain entanglement density tend to deform by crazing (examples are polystyrene, poly(methyl methacrylate) and poly(styrene-co-acrylonitrile)). Poly(vinyl chloride) has an intermediate chain entanglement density. Shear yielding is the main toughening mechanism for PVC when toughened by rubber.[64] Crazing is the deformation mechanism when the entanglement density of the polymer is below a certain critical value. At higher entanglement densities both crazing and shear yielding take place.[65] Entanglements strongly influence the dynamic properties and the glassy state properties such as viscosity and toughness.[65]

The motion of polymer chains is dominated by the presence of direct polymer chain-polymer chain interactions or entanglements in nondilute solutions.[66] The increase in specific viscosity is associated with the more numerous entanglements and stronger interactions between the polymer chains which leads to a more extensive energy dissipation. The density of entanglement coupling is independent of the solvent nature at higher concentrations.[66]

Shape memory results from crystalline structure, glassy state, entanglements, and/or crosslinking.[67] Because PVC has low crystallinity, its shape memory is mostly controlled by actual entanglement density (for example, if entanglement density decreases during exposure to UV also its shape memory fails). To increase shape memory in PVC, crosslinking is used.[67]

3.6 CRYSTALLINE STRUCTURE

Structural studies are usually associated with results obtained by X-ray diffraction. Natta and Corradini[68] have measured the unit-cell dimensions as follows: a=1.06 nm, b=0.54 nm and c=0.51 nm. The space group is Pcam, Z=4 and the unit cell is orthorhombic. These data have been confirmed later by Wilkes.[55] Each cell contains two PVC chains arranged in planar zig-zag conformation, with the c direction corresponding to two chemical repeat units. Since lengths of syndiotactic sequences are on average no more than 5–6 repeat units, crystallites in the c direction are very thin.[69] The amorphous trace for PVC has two broad diffraction peaks. The first one at d=0.36 nm corresponds to van der Waals spacings between groups of atoms. The peak corresponding to d=0.50 nm has been attributed to

various types of chain packing in non-crystalline regions.[69] For a crystalline fraction, two main diffraction peaks are observed with Cu K_α radiation, superimposed on the amorphous background. The peak at $2\theta=16–18^o$ have been assigned to (110) and (200) planes, while at $2\theta=25^o$ there are overlapping peaks from (210), (201), and (111) planes.

X-ray studies are the most useful for highly crystalline materials of syndiotactic configuration. Similar data for industrial polymers are difficult to obtain because they have low crystallinity.

Assessing the crystallinity of polymer by wide-angle X-ray scattering measurement, we assume the two-phase concept of the polymer structure, i.e., we imply that there is a difference between the crystalline area and the amorphous area in the polymer sample and on a diffractogram. Therefore, the result of the crystallinity index depends greatly on how we choose the amorphous area. It is a common practice to use a quenched sample as an amorphous standard, but such sample has a profile similar to a crystalline diffraction pattern with diminished intensity by, let's say, the small size of its reflecting crystallites. It will be interesting to quote in full Guerrero's[70] comments on this subject:

> Under these circumstances it is difficult to surmise what the true shape of amorphous scattering in PVC will be. There are serious doubts as to the validity of the widely accepted quenched PVC amorphous profile. In any case, the presence of the intermediate state of order would certainly question even further the use of a simple two-phase concept to derive crystallinity values from PVC diffractometer curves.

These difficulties were experienced by this author[71] in studies carried out in 1970s, in which the crystallinity index was measured for about 20 samples of industrial polymers in order to use it as a factor characterizing their processability.

There are several other reasons which cause results that are uncertain. These are related to sample preparation which modifies:[72]

- the unit cell of PVC
- crystallite orientation
- mesomorphous content.

Several other methods can be applied in order to measure the crystalline nature of polymer. These are IR and Raman spectroscopy, density determination, DSC measurements, and deuterium NMR. Practical significance in PVC has IR spectroscopy and density determination. Deuterium NMR was used in one case[73] giving good comparative results, but estimated crystallinity was much higher (18%) than typically given by other methods.

Chartoff, *et al*.[74] characterized an internal order of PVC material by IR spectroscopy. This technique is frequently used, but the method of interpreting results is still under dispute. First of all, one should take into consideration that industrial polymers differ in their IR spectrum, particularly in the carbon-chlorine stretching region, where three bands are located at 610, 635 and 690 cm^{-1}. Also, not only the crystallinity of the sample affects IR absorption, but also the physical state, tacticity, history of the specimen, and so on. The

usual approach taken in IR studies is to compare the absorption intensity at the crystalline active frequency with that of the crystalline inactive band. The last band acts as an internal standard. In the early studies, absorption at 690 cm^{-1} was used as the internal standard, but it was soon discovered that this band is closely related to tacticity, and therefore, it cannot be regarded as a good reference band, since crystallinity and syndiotacticity are interrelated. The other possibilities were therefore exploited so as to use either absorption at 2920 or 2960 cm^{-1}, which are C-H_2 antisymmetric stretching mode vibrations and C-H stretching mode, respectively, and the previously mentioned band at 610 cm^{-1}. Considering the crystalline active absorbance, it seems that the 635 cm^{-1} frequency would be the most appropriate. From Chartoff's studies on spectral changes during annealing, it is evident that the ratio of A635/A610 serves the purpose of crystallinity determination.[74]

In more recent studies,[75-78] 604, 635, and 1427 cm^{-1} are considered crystalline bands and 615 and 1435 cm^{-1} are amorphous bands. Comparing Raman and IR data, 613 and 639 cm^{-1} crystalline bands were found useful.[79]

Density measurement is also a crystallinity indicator as it depends on the contribution of amorphous and crystalline phases. The average crystallinity value (X_c) can be calculated from the following formula:

$$X_c = \frac{d_c d_a / (d - d_c)}{d_a - d_c} \qquad [3.9]$$

where:

d_c	crystalline phase density,
d_a	amorphous phase density (determined in amorphous condition of sample),
d	density of a particular sample.

The density measurement is less sensitive than IR studies, and both methods suffer from difficulties in obtaining a standard of amorphous PVC. It was estimated[80] that the density of amorphous PVC was 1373 kg m^{-3} and density of crystalline fraction was 1530 kg m^{-3}.

There is full agreement that crystalline structures are formed from syndiotactic sequences. The syndiotactic sequences obtained from radical polymerization are usually short, but there are strong attractive forces between chains associated with the C–Cl dipoles that induce crystallinity.[46] Typical commercial PVC is polymerized at 50°C and it has about 30% of syndiotactic triads.[81] 5-10% crystallinity level is expected by a prevailing number of researches of PVC.

Two models of crystalline structures are commonly accepted: lamellar (Figure 3.5) and fringed micelle type (Figure 3.6). It is apparent from drawings that lamelar structure is better organized than fringed micelle type. Lamellar type of crystallites are believed to have higher melting temperature.[82] More likely, lamellar crystallites are formed during polymerization and they are main forms of the so-called primary crystallinity which is originally present in PVC powder grains after polymerization.[83] The lower the polymerization temperature the higher the syndiotacticity and the higher the crystallinity. Secondary crystallinity is formed on cooling after polymer was heated above the glass transition

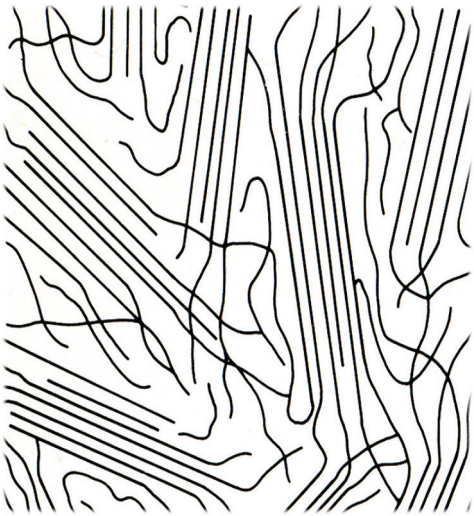


Figure 3.5. The fringed micelle model of crystallization.

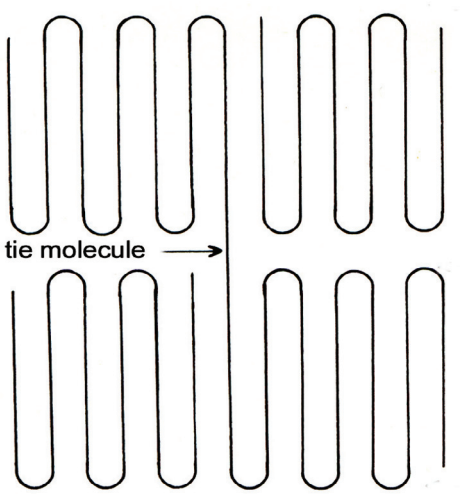


Figure 3.6. Lamellar structure of crystallite.

temperature. It has to be noted that there is no direct knowledge of morphological structure.[81]

Crystallites are very small and they have an average distance between crystalline regions of 10 nm. In order to form a network, crystallites need to be connected together by tie molecules. According to Summers *et al*.[84] PVC having K-value close to 50 has the average radius of gyration close to 10 nm. For K-values of 58 and 68 they estimated the radius of gyration to be approximately 13 nm and 20 nm, respectively.[85] There is still another explanation of the connectivity between crystallites by the fiberlike model which describes the molecular structure of PVC aggregates.[86] According to this model, fibrous crystals arise from the crystallization of rigid or semirigid chains and there are no fold chains in the crystals. The fiberlike morphology has also been experimentally observed in the PVC gels in good and bad solvents.

Figure 3.7. PVC spherulite. Adapted, by permission, from Dobreva, A.; Gantcheva, T.; Gutzow, I., *Cryst. Res. Technol.*, **27**, 6, 743-748, 1992.

Size of crystallites seems to depend on conditions of polymerization and sample preparation. It varies in a quite narrow range of 0.7 to 15 nm with spacing between crystallites from 0.5 to 20 nm. There is almost full agreement that PVC does not form spherulites because of the small size crystals. But there is an exception in one paper according to which small spherulites are formed (see Figure 3.7).[87] This result of research should be treated as a specific case because research material was obtained under specific conditions of catalyzed nucleation on special crystallization cores.[87]

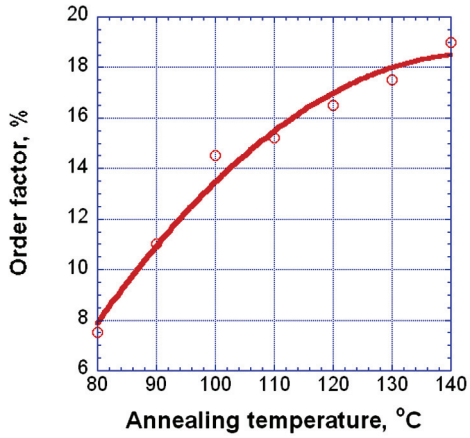


Figure 3.8. Effect of annealing temperature on the order factor in PVC. [Data from Liu, Z.; Gilbert, M., *Polymer*, **28**, 1303-1308, 1987.]

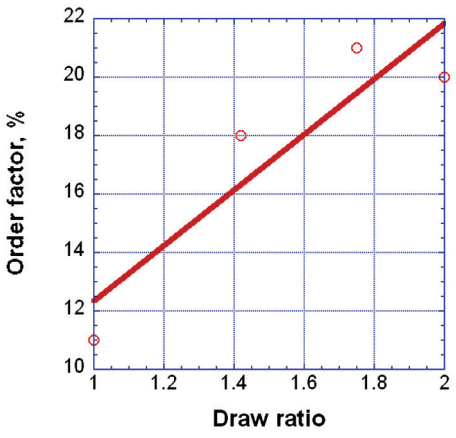


Figure 3.9. Effect of drawing on the order factor in PVC. [Data from Liu, Z.; Gilbert, M., *Polymer*, **28**, 1303-1308, 1987.]

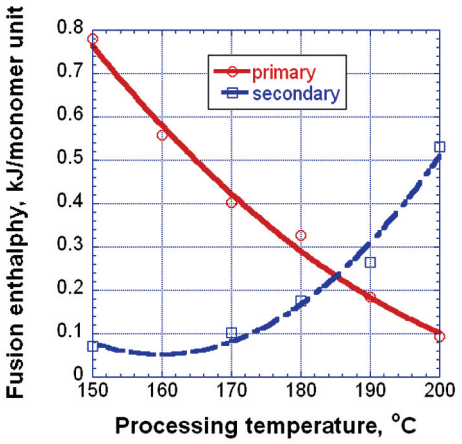


Figure 3.10. Effect of processing temperature on fusion enthalpy of primary and secondary crystallites. [Data from Li, T.; Qi, K., *J. Appl. Polym. Sci*., **63**, 13, 1747-1754, 1997.]

The theoretical melting point of a perfectly syndiotactic PVC is estimated to be about 400°C, but such a polymer has not been synthesized.[46] The melting points of PVC synthesized by radical polymerization are 102–230°C because of small size crystallites and imperfections in the ordered structure.

Temperature and orientation are the most influential factors which impact secondary crystallization (the number of crystallites, their structure and size, and their spatial distribution and interaction). Figures 3.8 and 3.9 show effect of annealing temperature and draw ratio on order factor.[88] It is well established that drawing increases tensile strength and elongation of material.[88-91]

The presence of crystallites is very important for product performance because they serve as physical crosslinking points which reinforce material and improve its viscoelastic properties. It is therefore very important to notice that the mechanism peculiar to PVC allows for melting of crystallites and their formation on cooling. Melting crystallites improve their processability, and their recovery improves performance characteristics of PVC. Heat of crystallite melting is 74 kJ kg^{-1}.[73] Figure 3.10 shows effect of processing temperature on fusion enthalpies of primary and secondary crystallites.[92] The gelation

degree was estimated based on the melting enthalpies of primary and secondary crystallites according to the following formula:[93]

$$G = \frac{H_p}{H_p + H_s} \times 100\% \qquad [3.10]$$

where:

G	gelation degree of PVC as estimated by DSC
H_p	melting enthalpy of primary crystallites
H_s	melting enthalpy of secondary crystallites

Several other factors were found to affect crystallinity. Milling is one such factor, although it is not clear whether crystallinity is increased or decreased by milling. In one study,[88] both crystallinity and crystallite size were increased when PVC mixed with thermal stabilizers was milled at 165°C.[88] Authors attributed this growth to combination of shear effects and intergrain crystallization. In another study,[82] the effect of vibromilling and jet milling on gelation was investigated. Apparent density and crystallinity of PVC measured by infrared were decreased during milling.

The effect of plasticizer on crystallinity is not fully understood. In one study,[94] addition of DOP did not affect crystallinity up to 50% concentration. In another study,[77] the effect was dependent on compatibility of plasticizer (more compatible plasticizers decrease crystallinity more extensively). It seems that if there is such effect it is negligible because plasticizer cannot easily penetrate crystalline domains.

UV degradation was found to increase crystallinity as measured by infrared.[95] It is suggested that crystallinity increased because of degradation of the amorphous phase.

Crystallinity affects many properties of PVC. We have already discussed the effect on density, antiplasticization, fusion, tensile, and elongation. Crystallinity also affects dehydrochlorination during UV exposure.[96] Since degradation occurs at temperatures below the glass transition temperature, crystalline domains remain unaffected and degradation occurs in the amorphous phase.

The physical aging of PVC is affected by the degree of crystallinity.[97] The effect is not only restricted to the overall percentage of crystallinity, but also to the entire structure of the material. It seems that the quality of crystallites influences the structure of the amorphous phase (i.e., the extent of disturbed regions, as well as the segmental mobility of undisturbed regions) which is responsible for the aging phenomena.[97]

3.7 GRAIN MORPHOLOGY

3.7.1 STAGES OF MORPHOLOGY DEVELOPMENT DURING MANUFACTURE

3.7.1.1 Suspension polymerization

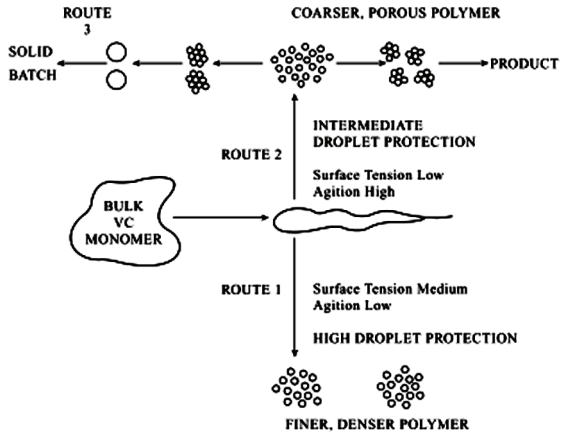


Figure 3.11. Particle formation in PVC suspension polymerization. [Adapted, by permission, from Allsopp, M. W., *Pure Appl. Chem.*, **53**, 449–65, 1981.]

Suspension polymerization includes fours main steps: polymerization, stripping residual vinyl chloride, centrifugation of water suspension to remove water, and drying. It is easy to predict that each of these processes influences morphology. Details of the manufacture technology are included in Chapter 2.

The first set of influences is related to the selection of formulation, method of addition of components, and agitation. Some of these influences are included in commonly used diagram (Figure 3.11).[98] Monomer droplets dispersed in water polymerize into PVC particles by one of three different routes differing by the agitation intensity and the stability of the protective colloid.

Route 1 includes use of protective colloid with medium surface tension in combination with weak agitation. Dispersed particles keep their small size during polymerization and change to the fine and dense PVC particles.

Route 2 includes use of protective colloid with low surface tension in combination with intensive agitation. Dispersed particles agglomerate by collision and form coarser particles with high porosity.

Route 3 shows an improper conditions, such as too strong agitation or inadequate droplet protection.[99]

Grain size can be modelled using Taylor's equation or its modification:[99]

$$a = \frac{16\sigma}{\gamma\eta}\left(\frac{\eta' + \eta}{19\eta' + 16\eta}\right) \qquad [3.11]$$

$$a = \frac{K\sigma G^{0.2}}{(\gamma\eta)^{1.2}}\left(\frac{\eta' + \eta}{19\eta' + 16\eta}\right) \qquad [3.12]$$

where:

a	radius of droplet,
σ	interfacial tension,
γ	rate of shear,
η'	viscosity of fluid in the droplet,

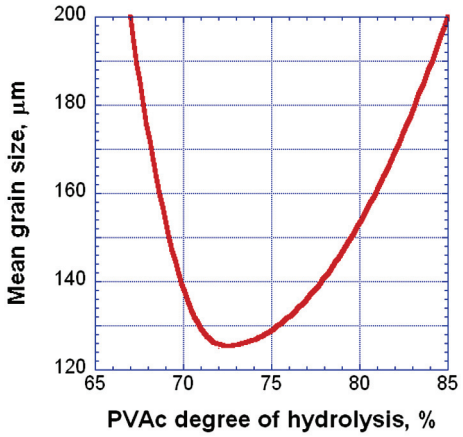


Figure 3.12. The effect of PVAc hydrolysis degree on PVC grain size. [Data from Zimmermann, H., *J. Vinyl Additive Technol.*, **2**, 287–94, 1996.]

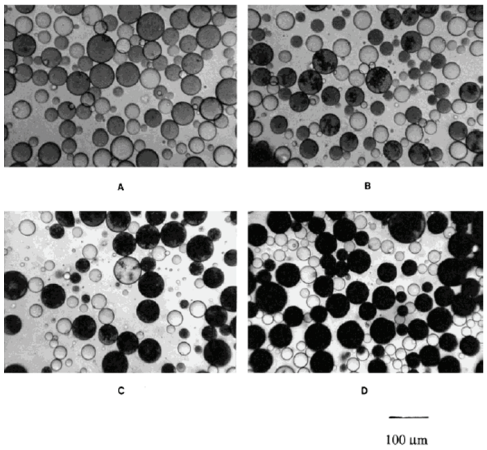


Figure 3.13. Changes occurring in vinyl chloride droplets during early stages of suspension polymerization. (A) 5 min, (B) 10 min, (C) 20 min, (D) 60 min. [Adapted, by permission from Zerfa, M.; Brooks, B. W., *J. Appl. Polym. Sci.*, **65**, 1, 127-134, 1997.]

η	viscosity of continuous phase,
K	coefficient,
G	interfacial gel strength of hydroxypropyl methyl cellulose measured by penetrometer.

Polyvinyl acetate is the most commonly used suspending agent. Figure 3.12 shows that its degree of hydrolysis controls grain size.[100] Figure 2.10 shows that the grain porosity linearly decreases with the degree of PVAc hydrolysis increasing. Figures 2.7, 2.8 and 2.9 show effect of conversion on mean pore diameter, porosity, and specific surface area, respectively. Figure 2.2 shows the effect of agitator speed on agglomeration.

Figure 3.13 shows morphology of early stages of polymerization.[101] Photograph A (0.1% conversion) shows that stable and uniform primary particles are formed. Particles are stabilized by electrostatic forces. Photograph B (2% conversion) shows particles which reached a critical size above which particles coagulate. Particles on Photograph B begin to become darker because of progress of polymerization. Photograph C (conversion 4.5%) shows that most primary particles coagulated and polymerization continues. Photograph D (conversion 20.6%) shows close packing of primary particles. The shape of final PVC particle is defined at this point. It should be pointed out that suspending agent has strong influence on this stage. Particle uniformity is also controlled by method of addition of initiator.[101]

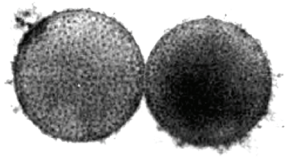


Figure 3.14. Precipitation of PVC in its own monomer at low conversion. [Adapted, by permission from Summers, J. W., *J. Vinyl Additive Technol.*, **3**, 2, 130-139, 1997.]

Summers[102] shows an interesting photograph (Figure 3.14) from early stages of polymerization. At less than 2% conversion in suspension and mass polymerization, PVC begins to precipitate because polymer is insoluble in mono-

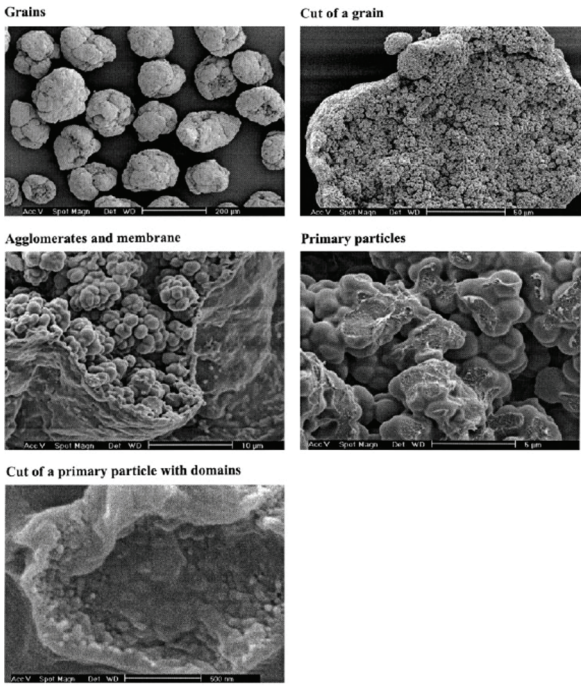


Figure 3.15. Morphology of PVC grains. [Adapted, by permission from Diego, B.; David, L.; Girard-Reydet, E.; Lucas, J.-M.; Denizart, O., *Polym. Intern*., **53**, 5, 515-522, 2004.]

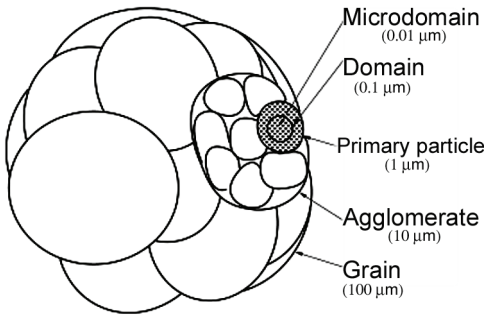


Figure 3.16. Model of PVC grain. [Adapted, by permission, from Saeki, Y., *Kagaku Keizai*, **47**, 11, 78–86, 2000.]

mer, which is unique feature of PVC polymerization (most polymers are readily soluble in their monomers).[102]

Figure 3.15 shows morphology of suspension PVC at its final stage. The PVC grains obtained by suspension polymerization exhibit a hierarchical morphology. They are constituted from agglomerates trapped inside a skin made of hydrosoluble polymers. The agglomerates are made out of primary particles. Inside the primary particles, domains are visible.[103] This peculiar morphology of PVC was described by Geil[104] over 30 years ago and since that time this nomenclature is consistently used to describe properties or features of suspension PVC morphology.

Figure 3.16 shows a schematic diagram of suspension PVC grain.[105] It compares very well with features of PVC micrographs in Figure 3.15. The details of morphology are discussed in Table 3.4 which includes modifications made by Allsoop[106] to improve the original Gail's nomenclature.

Table 3.4. Suspension PVC nomenclature. (Based on refs. 104-106)

Structural element	Size range, μm	Description
Grain	50-250	Visible constituent of free flowing powder
Agglomerate	1-10	Formed by coalescence of primary particles as shown in Figure 3.13
Primary particle	0.5-1	Grown droplet of monomer
Domain	0.1-0.2	Formation of inside of primary particle visible only at conversions below 2%
Microdomain	0.01-0.02	Smallest visible particle made out of approximately 50 chains. It is not visible at conversions higher than 2%

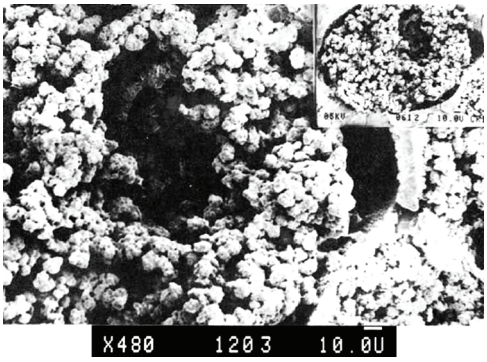


Figure 3.17. Membrane (skin) surrounding PVC particle. 480x. [Adapted, by permission, from Cebollada, A. F.; Schmidt, M. J.; Farber, J. N.; Capiati, N. J.; Valles, E. M., *J. Appl. Polym. Sci*., **37**, 145-166, 1989.]

Table 3.4 omits one essential component of suspension PVC structure, which is skin. Skin is formed on the surface of the PVC grains because the surface of the VC droplets is in contact with an aqueous phase and absorbs dispersant dissolved in water at the initial stage of polymerization and graft copolymerization with vinyl chloride and dispersant occurs.[107] Daniels mentions a skin-like membrane, thought to originate from the dispersant used in the polymerization.[108] Cuthbertson *et al*.[109] point out that poly(vinyl alcohol) is added to the polymerization recipe to prevent coalescence of PVC particles swollen by monomer, and that it functions by coating the particles with a skin. This explanation does not explain presence of skin which engulfs the entire grain as seen in Figure 3.15. Nakajima and Harrell[110] offer the opinion that the suspending agent, to which PVC microdomains are attached, forms a skin layer on the grain. Inside of the skin layer are the subparticles and interconnected pores.[110] Shah and Poledna[111] conclude that since conventional suspension polymerized PVC has a pericellular membrane (skin), the skin can impede the absorption of plasticizer. Summers[102] concludes that early in the polymerization, particles of PVC deposit onto the membrane from both the monomer and the water sides forming a skin 0.5-5 μm thick that can be observed on grains after polymerization.

There is no question about the presence of such membranes (skins) in many suspension grades since we can see them on SEM photomicrographs (Figure 3.17).[112] Based on the above observations, we may conclude that all information points in the same direction: that the skin is formed due to the presence of suspending agent; but it is also clear that we do not know the composition of the skin (whether it is PVC, VC-VAc copolymer, or

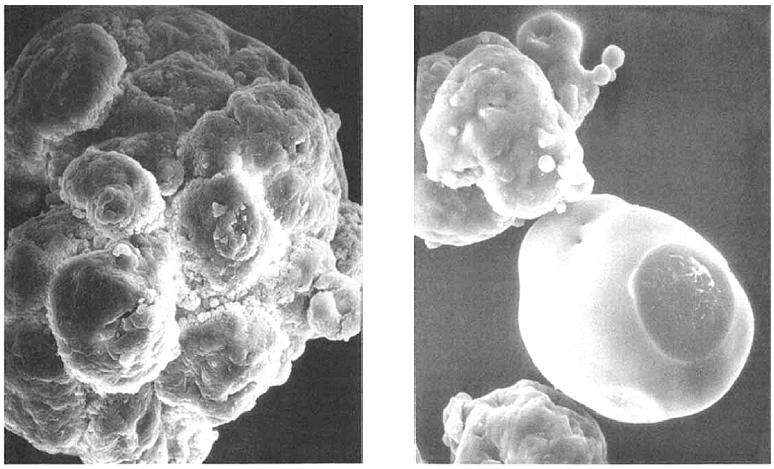


Figure 3.18. Suspension PVC particle (A) and particles exposed to 200°C (B). [Adapted, by permission, from Rabek, J. F.; Lucki, J.; Kereszti, H.; Hjertberg, T.; Jun, Q. B., *J. Appl. Polym. Sci.,* **39**, 1569-1586, 1990.]

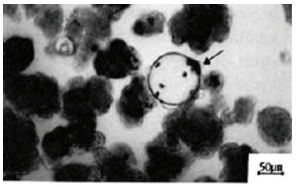


Figure 3.19. Photograph of a clear particle responsible for "fish-eye" formation. [Adapted, by permission, from Arslanalp, C.; Erbay, E.; Biligic, T.; Savasci, O. T., *Angew. Makromol. Chem.*, **193**, 3321, 99-112, 1991.]

PVAc). It is more likely one of the last two, since skin affects fusion and plasticizer penetration.

It should be pointed out that thermal treatment (e.g., drying) also affects PVC morphology. Figure 3.18 shows that the surface of grains was melted.[113]

Figure 3.19 shows clear particles which were found to cause "fish-eyes".[114] "Fish-eyes" are solid, unmelted looking small spots which may be formed due to various reasons (in the case of PVC, large PVC particles, less porous and/or usually clear particles of all PVC, and contaminations in PVC, which do not melt under test conditions).[114]

When suspension PVC was dissolved in tetrahydrofuran and dropwise added to methanol to precipitate PVC, its morphology was drastically changed.[115] The original grain structure and skin were destroyed.[115] Resulting polymer required more time to melt because PVC grains caused self-heating which increased temperature faster on mixing.[115] At the same time, precipitated polymer had much higher absorption of plasticizer due to its substantially smaller bulk density and more developed structure.[115]

Due to very complex morphology, it is very difficult to determine particle size distribution of suspension PVC. Comparative studies show that application of image analysis in determination of particle size gives a lower error compared with other methods.[116-117]

3.7.1.2 Paste grades manufacture

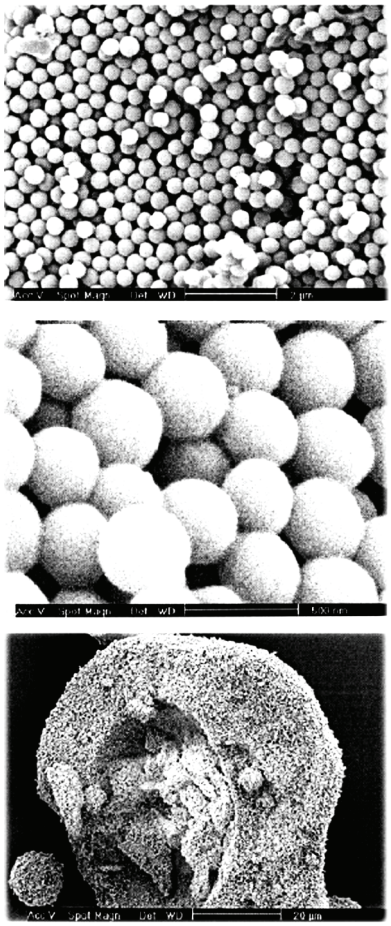


Figure 3.20 Morphology of emulsion PVC. [Adapted by permission, from Diego, B.; David, L.; Girard-Reydet, E.; Lucas, J.-M.; Denizart, O., *Polym. Intern*., **53**, 5, 515-522, 2004.]

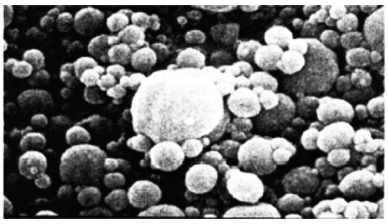


Figure 3.21. Morphology of microsuspension PVC. [Adapted, by permission, from Shah, A. C.; Poledna, D. J., *J. Vinyl Additive Technol*., **9**, 3, 146-154, 2003.]

Paste grades are manufactured by emulsion and microsuspension polymerizations. The production includes the following unit operations: charging, premixing, and homogenization (only microsuspension polymerization), charging and polymerization, stripping, spray drying, separation, grinding, screening, and packaging (for more details see Chapter 2). Much smaller particles are produced as a result of these processes as compared with suspension polymerization.

Figure 3.20 shows morphological features of emulsion PVC at different magnifications. Particles are very small (0.1 to 0.3 μm) and they have regular shape. Morphology of emulsion PVC is simple because of spherical shape of its particles and of narrow particle size distribution. Drying process may introduce some variations in morphology because of partial surface melting and agglomeration of particles. Mean particle size and particle size distribution of paste resin, which have direct relation to production process, are the important factors for controlling properties of plastisol. The larger mean particle size produces the lower viscosity plastisol. Also, particle size distribution of paste resin affects rheological characteristics of plastisol.

Figure 3.21 shows a photograph of paste resin manufactured by microsuspension polymerization. It is pertinent from this photograph that microsuspension resins have much less regular particles and wider particle size distribution (0.1 to 5 μm). The particles obtained in the course of polymerization may still agglomerate during drying. The agglomerates may have a mean particle size of 30 to 60 μm which is subsequently reduced to 5 to 20 μm by milling.[99]

Blending resins are also used in paste processing. These resins are manufactured by suspension polymerization. They have all the morphological features of suspension resins except for particle size, which is between 25 and 75 μm (several times smaller than typical suspension resin).[118] Blending resins are not dried by spray drying like the other two types; rather, rotary fluidized bed drying is used. Most of the water can be removed by centrifugation because their particles are large enough to not block filters.[118] This means that lower exposure to high temperatures can be expected during drying of blending resins. Since blending resins are porous they are capable of absorbing plasticizer and they are used to regulate flow properties of plastisol and concentration of plasticizer.

3.7.1.3 Bulk polymerization

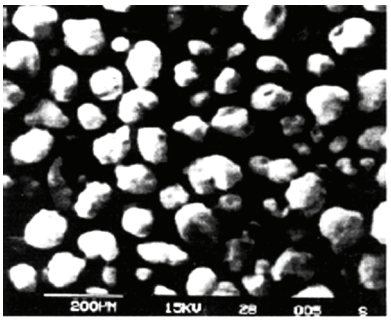


Figure 3.22. Morphology of bulk polymerized PVC. [Adapted, by permission, from Luo, Y.; Dai, G., *J. Appl. Polym. Sci*., **86**, 3331-3335, 2002.]

The formulation of bulk polymerization is the simplest because it includes only monomer and initiator. This eliminates processes of separation from water, drying, and contaminating additives (more details of the process can be found in Chapter 2).

Figure 3.22 shows morphological features of bulk PVC. Particle shape is a result of a milling process. Particle size is similar to the suspension resins but particle size distribution is usually very narrow. There is no barrier to plasticizer and other liquids' diffusion because there is no skin similar to suspension PVC and there is no melted surface as is the case of other resins because they are subjected to heat during drying. Also, polymer is almost pure PVC containing only rests of initiator and typical defects related to polymerization, but there is no suspension or emulsion agents which may affect degradation rate, diffusion of plasticizer, and fusion processes.

3.7.1.4 Nonaqueous polymerization

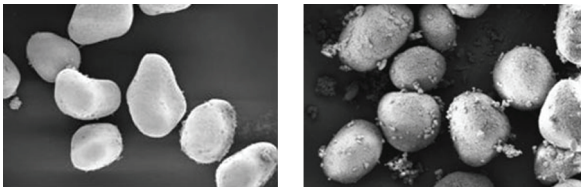


Figure 3.23. Examples of PVC morphology obtained by nonaqueous polymerization. [Adapted, by permission, from Georgiadou, S; Thomas, N. L.; Gilbert, M.; Brooks, B. W., *J. Appl. Polym. Sci*., **112**, 2472-81, 2009.]

Elimination of waste water, energy savings, and reduction of carbon dioxide reduction was achieved by polymerization of vinyl chloride in hexane.[120] The nonaqueous process leads to PVC grains with higher porosity, slightly lower bulk density and no effect on thermal stability as compared with regular suspension PVC.[120] The porosity of the nonaqueous PVC is significantly higher than that of the suspension PVC.[120] The type of suspending agent had a strong influence on the shape and morphology of the polymer particles, similar to regular suspension polymerization process.[120] Figure 3.23 shows some morphologies obtained with different suspension agents.[120] On the left, nonaglomerated

particles were formed with smooth, even grain surface.[120] On the right, almost spherical particles were produced with some agglomeration.[120]

3.7.2 EFFECT OF MORPHOLOGY ON DEGRADATION

Trapping of HCl is potentially the most important influence on PVC degradation. Cuthbertson *et al*.[109] studied the effect of the concentration of suspending agent (PVAc) on dehydrochlorination. They concluded that the thicker skin of the 1000 ppm PVAc polymerization traps more hydrogen chloride liberated during the annealing process and this causes autocatalytic processes during the following stages of degradation. The presence of hydrogen chloride leads to longer polyene sequences and this is the most plausible explanation for the differences observed with the two PVAc levels.

Kip *et al*.[31] argued that the polyene sequence distribution might not be the same for the skin and core of the PVC grains. Braun *et al*.[121] believe that sample morphology may affect dehydrochlorination rate. Formation of film by pressing affected the formation of polyenes as compared with free powders, which was attributed to changes in morphology and restriction of HCl removal.[122]

These few contributions do not carry sufficient experimental material for direct proof of influence of morphology on dehydrochlorination. It is due to the fact that it is difficult to design an experiment which will separate this influence from many other influences which cause dehydrochlorination. At the same time, there should be no doubt that HCl diffusion process from porous grains of bulk and, especially, suspension polymer meets many obstacles due to the tortuosity of its pathways. This has to be factored in modelling processes of degradation and stabilization.

In addition to morphology created by polymerization, we may also expect that structural damage and formation of skin on the surface of particles during their drying will influence dehydrochlorination rates due to the formation of defects and lower diffusion rate of HCl, respectively.

We may also consider that the heat required for melting crystallites increases the duration of fusion processes. Also, any other obstacle to fusion, such as, for example, skin on the surface of particles or coating by residual emulsifier, will affect exposure to thermal treatment and it will affect the extent of thermal degradation.

Finally, we should also consider that complex morphological structures affect distribution of stabilizers because they do not act in a homogeneous manner and decrease thermal stability of PVC.

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4

Principles of Thermal Degradation

4.1 THE REASONS FOR POLYMER INSTABILITY

Chapter 1 contains all information available on formation mechanisms and concentration of various structural defects in the PVC chain. Here we discuss known information on the mechanisms of initiation of PVC thermal degradation by these labile structures. The chapter also discusses other chemical influences caused by the presence of various chemical rests and additives introduced during polymerization, impurities, metal derivatives (those potentially present in the original polymer and formed from polymer additives, most importantly thermal stabilizers) during degradation as well as physical conditions of degradation such as molecular mobility, temperature, atmosphere, and mechanical forces.

4.1.1 STRUCTURAL DEFECTS

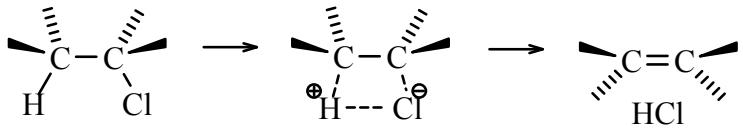
4.1.1.1 Branches

Branches do not cause PVC instability if hydrogen is substituted at the tertiary carbon atom but they form labile groups if chlorine is substituent of the tertiary carbon atom (see the next section). The only other influence of branches on dehydrochlorination rate can be associated with their influence (long branches) on the entanglement density (see previous chapter).

4.1.1.2 Tertiary chlorine

Tertiary chlorine is considered as one of the most important defects which increases the dehydrochlorination rate. Some scientists[1-3] consider it to be the most influential initiator of the dehydrochlorination process because this defect is present at high concentrations.

Based on the studies of low molecular models, Bacaloglu *et al*.[3-6] postulated that elimination occurs by a four-center mechanism, as below:



The rate constant of HCl elimination for tertiary chlorine is 1.75×10^{-3}, and for secondary chlorine, 5.0×10^{-7}, which shows that tertiary chlorine is more reactive than secondary chlorine.[5] Similar conclusions come from results of calculation by MNDO and AM1 which show that activation energy of dehydrochlorination of tertiary chlorine is

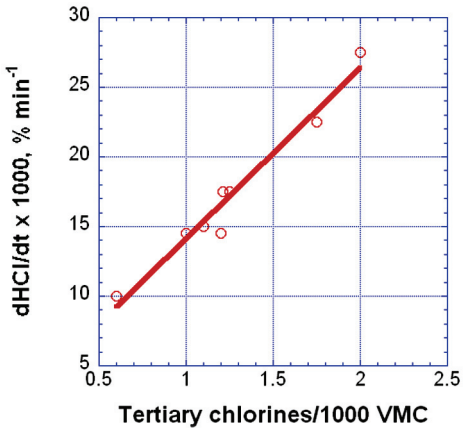
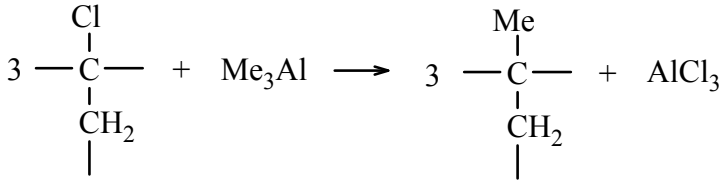


Figure 4.1. Effect of tertiary chlorines on PVC dehydrochlorination rate. [Adapted, by permission, from Xie, T. Y.; Hamielec, A. E.; Rogestedt, M.; Hjertberg, T., *Polymer*, **35**, 7, 1526-34, 1994.]

much lower than that of secondary chlorine.[7] Also, bond energy of C-Cl attached to the tertiary carbon atom is lower by 10 kcal/mol compared with chlorines attached to the secondary carbon atoms.[8]

The synperiplanar four-center transition state is forbidden by Woodward-Hoffmann rules. Consequently, in order for it to occur, a non-simultaneous mechanism requiring strong polarization of the C-Cl bond must prevail. Experimental data and theoretical calculations support the predicted polarization. At the same time, this slows down reaction rate.[4] Highly polar solvents ionize tertiary chloroalkanes, changing the mechanism of elimination to a process which requires lower activation energy.[4]

The effect of tertiary carbon atoms on the initiation of dehydrochlorination was confirmed by experiment in which tertiary chlorines were eliminated by the reaction with trialkyl aluminum, as follows:[9]



PVC reacted with trimethyl aluminum had a reduced rate of dehydrochlorination.[9]

Figure 4.1 shows the effect of concentration of tertiary chlorines in PVC on its dehydrochlorination rate.[2] Using linear regression, the following equation was obtained from the data in Figure 4.1:[2]

$$\frac{dHCl}{dt} = 3.3 + 12.4[Cl]_T \ \ 10^{-3} \ min^{-1} \qquad [4.1]$$

where:

dHCl/dt	dehydrochlorination rate,
$[Cl]_T$	tertiary chlorines/1000 VMC.

This data shows that there is little doubt that tertiary chlorine atoms are capable of initiation of PVC dehydrochlorination. Bacaloglu *et al.*[3] pointed out that initial rate of decomposition of PVC is higher because of the presence of tertiary chlorines and it later slows down when they are exhausted. This seems to coincide with observations from PVC degradation testing during which initial emission of HCl is indeed more extensive and it

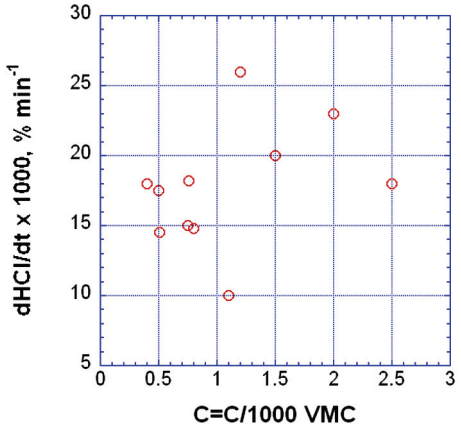


Figure 4.2. Effect of concentration of internal double bonds on dehydrochlorination rate. [Adapted, by permission, from Xie, T. Y.; Hamielec, A. E.; Rogestedt, M.; Hjertberg, T., *Polymer*, **35**, 7, 1526-34, 1994.]

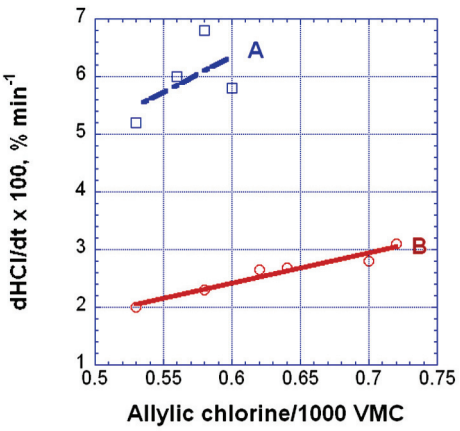


Figure 4.3. Effect of concentration of chloroallyl groups on dehydrochlorination rate. [A – data from Dean, L.; Dafei, Z.; Deren, Z., *Polym. Deg. Stab.*, **22**, 31-41, 1988; B – data from Xu, P.; Zhou, D.; Zhao, D., *Eur. Polym. J.*, **25**, 6, 575-579, 1989.]

eventually slows down to produce a constant degradation rate during the phase of polyene extension. This initial increase may also be caused by the fact that HCl is removed from the sample by diffusion in the beginning but later, when its concentration rises, the sample becomes porous, which suddenly increases HCl output.

4.1.1.3 Unstaturations

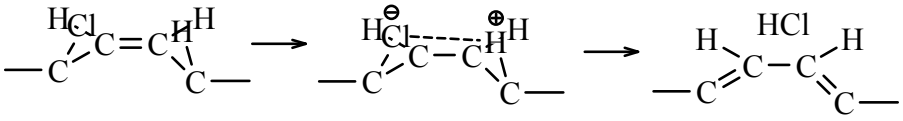
Unsaturations alone do not increase the rate of initiation but there is common agreement that internal double bonds, due to the presence of chloroallyl groups, may serve as active initiation centers of dehydrochlorination. Chlorallyl groups and tertiary chlorines are the most important defects which initiate thermal degradation.[1] Unsaturations at the chain ends have no effect on polymer thermal stability.[10-11]

Minsker *et al*.[10] claimed that chloroallyl groups rapidly oxidize to ketochloroallyl groups and that they contribute to chain reaction initiation, but this has not been accepted and it is not considered valid.

Chloroallylic bond between chlorine and carbon has energy of 58 kcal/mol compared with the same bond in tertiary chlorine having energy of 67 kcal/mol.[8] The constant of dehydrochlorination is 1.17×10^{-3} for allylic chlorine and 1.75×10^{-3} for tertiary chlorine.[5] This shows that chloroallyl groups are better initiators of thermal degradation but at the same time they are less numerous. Figure 4.2 shows that there is no correlation between chloroallyl concentration and the rate of thermal degradation. This indicates that there are more influential factors (e.g., concentration of tertiary chlorines, see Figure 4.1) which affect degradation rate. Figure 4.3 shows otherwise, which may suggest that the influence of allylic groups is determined by the conditions of synthesis, especially taking into consideration that the formation of internal double bonds is independent of conversion, whereas concentration of tertiary chlorines rapidly increases above 70% conversion.[2] This

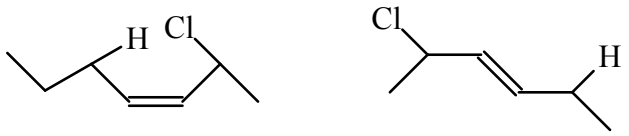
permits combinations with exaggerated influence of chloroallyl groups such as presented in Figure 4.3, but the stability of the general purpose, commercial PVC, is more influenced by tertiary chlorine than by the chloroallyl group. It should be noted that analytical methods and methods of defect calculation were different in all three cases reported.

Fisch and Bacaloglu,[14] based on studies of low molecular weight models, proposed a six atom transition state which lowers energy of dehydrochlorination of allylic chlorine:



Unlike the four-member state which also explains the mechanism of dehydrochlorination, this state is not forbidden by Woodward-Hoffmann rule and reaction occurs faster.

Geometric isomerism (see Chapter 3) is important in explanation of reaction mechanism and rate. Chemical structures below show explicitly why *cis*-configuration is reactive (H and Cl are in proximity) and why *trans*-configuration causes interruption of the dehydrochlorination chain of reactions:[3]



cis reactive **trans stable**

Cis-allylic chlorine is eliminated much faster[15] (about 50-200 times faster than *trans*).[4] Bacaloglu *et al.*[16] concludes that the chain of dehydrochlorination stops when it meets *trans* configuration on its way. *Trans* form has higher activation enthalpy and it is not considered to be an initiator of dehydrochlorination.[3] It is also possible that *trans*-configuration isomerizes in solution to *cis*-configuration.[4]

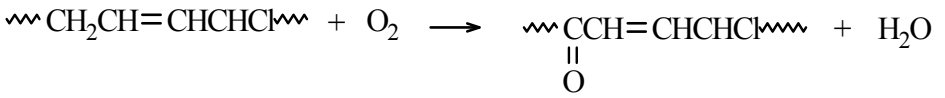
It should be pointed out that chloroallylic group is also very essential during propagation of dehydrochlorination and *cis-trans* isomerism may be a possible explanation of growth termination of polyene chains.

When polymer is exposed to the thermal processing as in the case of drying or reprocessing of waste polymer, large number of conjugated double bonds are formed in such polymer. This exposure and formation of conjugated double bonds dramatically decreases thermal stability as was experimentally confirmed.[17] When polymer lost 0.4 mol% of HCl due to the exposure for 30 min at 200°C, its onset decomposition temperature was 50-60°C lower than that of virgin resin.[17]

4.1.1.4 Oxygen containing groups

4.1.1.4.1 Ketochloroallyl

The possibility of the initiation of the dehydrochlorination process by chloroallyl groups was questioned by Minsker[10,18-20], who proposed that chloroallyl groups are rapidly oxidized into carbonyl-chloroallyl structures:



which are responsible for initiation of the dehydrochlorination process. The content of these groups depends on monomer purity, the presence of oxygen, and the temperature of the vinyl chloride polymerization process.

Caraculacu,[21] discussing this assumption, provided information on the model substances consisting of 4-chlorohexene-2 together with its transposed derivative 2-chlorohexene-3, which were not oxidized to the corresponding keto-chloroallylic structures even after one year of standing in air or oxygen.

Most current studies do not include this group on the list of important defects which have the potential to initiate dehydrochlorination.[22-26] Braun[24] even concluded that this group may have a decelerating effect on initiation of dehydrochlorination. Only Bacaloglu *et al*.[3-5] consider this group as a potential initiator of dehydrochlorination but they merely repeat information without offering any new supporting details.

In addition, there is no proof that these groups are present in commercial PVC at measurable concentrations.

4.1.1.4.2 Carbonyl

If a C=C bond can weaken a C-Cl bond in the β-position, the same effect may be expected when a double bond is formed between the carbon atom and oxygen in the vicinity of a C–Cl bond. It is known that carbonyl groups formed during photodegradation increase further degradation rate, therefore the same should be true for initiation of thermal degradation.

Using carbon monoxide copolymers of vinyl chloride, it was confirmed by experiment that the thermal degradation rate increased with increased concentration of carbonyl groups.[27] Rabek *et al*.[28] list carbonyl, aldehyde, hydroperoxide groups, which according to them can be formed in PVC during polymerization in the presence of air but no measurable quantities of any of these groups have been detected so far. It can therefore be concluded that carbonyl groups can potentially be initiators of dehydrochlorination, but because they are not present in commercial polymers (unless specifically required as in environmentally degradable polymers), they are not considered as defects of structure which may initiate dehydrochlorination.

4.1.1.5 Head-to-head structures

Murayama[29] showed that head-to-head PVC degrades at a lower temperature, but the rate of dehydrochlorination is higher for the head-to-tail form, which was also confirmed by Crawley,[30] although the differences between the two forms were not great.

Some earlier research[28] and a review paper[31] include head-to-head structures on the list of dehydrochlorination initiators, other review papers[26,32,33] include head-to-head structures on the list of defects but do not consider them as potential sites for initiation of dehydrochlorination. There is no recent experimental evidence or results of theoretical calculations which suggest that they may be less stable than the regular chlorines from head-to-tail addition.

The mechanism of head-to-head polymerization explains formation of chloromethyl groups.[1] It is also possible that head-to-head structures after dehydrochlorination produce stable structures of –CH=CCl– type.[34] Their stability is caused by the resonance between π electrons of the double and C-Cl bond.

4.1.1.6 Morphology

Knowledge of polymer morphology is very essential for understanding processes and mechanisms of degradation. For this reason, Chapter 3 contains full discussion of available data. In addition, this chapter contains discussion of the dehydrochlorination initiation mechanisms with participation of four- and six-member transitional states which explain initiation rates by tertiary chlorine and chloroallyl groups. It is also important to review the termination mechanism discussed in this chapter with participation of *trans*-configuration of terminal groups in growing polyene sequence.

4.1.2 POLYMERIZATION RESIDUE

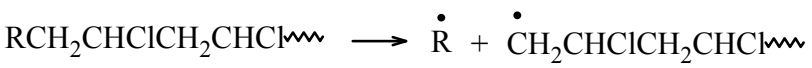
4.1.2.1 Initiator rests

Chain transfer to initiator is negligible. In most cases it occurs by chain transfer to monomer.[1] It is calculated that 4-5 chains of polymer are formed from one molecule of intiator.[33]

Two types of initiator were used in this limited comparison of their influence on dehydrochlorination.[34] Azobisisobutyronitrile had more pronounced influence on PVC dehydrochlorination than bis(4-t-butylcyclohexyl)peroxydicarbonate when all other factors stayed the same. Early color change increased if unreacted initiator was either left or intentionally added to polymer.[35] Increased concentration of initiator decreases thermostability of polymer.[36] It should be noted that commercial production can always prevent such occurrences.

The major goal of selection of initiator composition (see Chapter 2 for extensive discussion on this subject) is to increase production output.[37] But this is always optimized with product quality in mind, including thermostability (application of different initiator results at different concentration of tertiary chlorines and chloroallyl groups).[35,38] Initiator addition method also influences particle uniformity (particle size and shape influence time of heating).[39] There is no doubt that these factors are well controlled by manufacturers with the purpose of limiting their effect of dehydrochlorination.[26]

There are almost no data comparing different initiators in terms of their effect on thermal stability. One mechanism is proposed according to which initiator rests residing at chain ends may dissociate:[40]



the radical formed becomes mobile and it can readily abstract hydrogen causing formation of macroradical and thus increasing degradation rate.

In recapitulation, free initiator molecules and initiator rests can influence dehydrochlorination rate and its initiation but their performance and concentration are easily controlled, and most likely the initiators do not pose problems under normal conditions of PVC processing.

4.1.2.2 Transfer agent rests

Monomer is commonly used in practice as a chain transfer agent and does not influence PVC thermal degradation because it is a regular building block. In some cases,[41-43] chain-transfer agents are added to polymerization mixture mainly to control (reduce) molecular weight. Depending on their chemical composition, they may have no negative effect on dehydrochlorination (mercaptoethanol),[41] slightly increase degradation rate (dodecylmercaptan),[42] or rapidly increase degradation (formaldehyde).[43] Considering that these are mostly experimental products, a user of commercial products is typically not affected by their presence.

4.1.2.3 Polymerization additives

Suspension agents and emulsifiers are common additives found in polymerization recipes. Emulsifiers are known to modify flow properties,[44] affect viscosity changes over time,[45] affect results of K-number measurements (lower K-value by about 2 units),[46] and improve antistatic properties.[47] Suspending agents influence porosity and become part of the pericellular membrane, a skin encompassing particles of suspension PVC.[48]

There is no data or information on direct involvement of these additives in supporting degradative changes. It could be predicted that, since viscosity is influenced by temperature, any influence on viscosity will be corrected by temperature change; therefore these additives can be linked to indirect involvement in degradative processes. Also, formation of skin is related to problems with HCl diffusion as well as higher energy requirement to homogenize materials (fusion or gelation) before forming. This is also an example of indirect influence on degradative processes.

4.1.3 METAL DERIVATIVES

4.1.3.1 Metal chlorides

Metal chlorides discussed here are mostly products of reaction of thermal stabilizers with HCl. They remain in the material and they may influence the material's stability.

Calcium and barium chlorides

Calcium and barium are the next most electropositive metals after the alkali metals. Like the alkali metals, they form stable salts of which anions are the chief points of interest. The cations in salts have little deforming power, and hence they stabilize anions.

Figure 4.4. shows the effect of calcium stearate concentration on the induction period of PVC degradation.[49] The induction period is determined experimentally as the beginning of emission of HCl from PVC degraded under the nitrogen flow. Induction period is calculated from the equation derived by this author:[50]

$$n = \frac{PA}{v_0} \qquad [4.2]$$

where:

n	induction period,
PA	HCl absorption capacity of stabilizer (determined by conductometric titration),[50]
v_0	dehydrochlorination rate of PVC without thermal stabilizer.

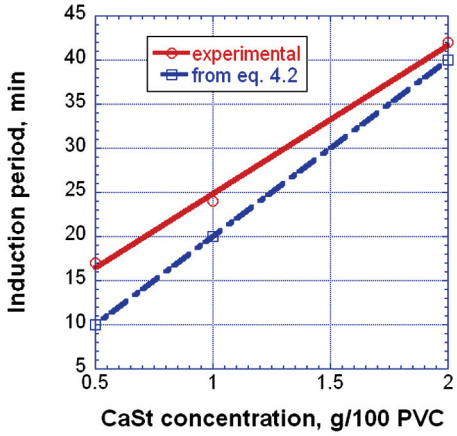


Figure 4.4. Induction period of PVC degradation vs. concentration of calcium stearate. [Data from Wypych, G., **Selected properties of PVC plastisols**, *Wroclaw Technical University Press*, 1977.]

Both experimental and calculated values give linear relationships but calculated results predict that degradation should have occurred faster. Equation 4.2 accounts for reaction of stabilizer but does not consider that unreacted HCl autocatalyzes PVC dehydrochlorination which is accounted for in experimental results. Figure 4.4 also shows that $CaCl_2$ (and none of intermediate products of reaction with HCl which could be formed) does not catalyze PVC degradation. Other metal chlorides that are thought not to influence the PVC dehydrochlorination rate are Na, K, Ba, Sr, Mg, Pb.[51-54] More recent publications either mention that $CaCl_2$ does not accelerate degradation,[55] or that calcium is more ionic and therefore does not increase degradation rate of PVC,[56] or that calcium chloride is not Lewis acid which explains why it does not catalyze dehydrochlorination.[57]

The above reported research does not answer questions regarding the mechanism of reaction with HCl, which can be schematically written as follows:

$$Ca(OOR)_2 + HCl \longrightarrow CaOORCl + ROOH$$

$$CaOORCl + HCl \longrightarrow CaCl_2 + ROOH$$

ROO = fatty acid rest

This scheme of reactions generates one essential question regarding the sequence of events. There are two possible scenarios:

- molecules of calcium stabilizer (calcium stearate or salt of any other fatty acid) react first with one molecule of HCl forming partially reacted stabilizer, CaOORCl
- molecules of calcium stabilizer react with two molecules of HCl forming final chloride, $CaCl_2$

Several studies were performed by this author,[58] including elemental analysis, IR spectroscopy, and x-ray analysis of samples of barium and calcium stearates reacted in moisture-free acetone with 50% of stoichiometric amount of HCl required to completely react with stabilizer. Elemental analysis of the product of reaction showed that its concentration of carbon, hydrogen, oxygen, chlorine, and calcium was very similar to concentration of these elements in CaClSt (BaClSt) and very different than concentration of these elements in calcium (or barium) stearates.[58] IR showed an additional peak around 1660 cm^{-1} which could not be attributed to stearic acid and was not present in the initial stearates.[58] By x-ray analysis it was possible to directly monitor concentration of the initial calcium stearate which was still present after addition of 35.6% stoichiometric quantity of HCl. Only after 81.3% of stoichiometric HCl was added, the peak for calcium stearate was not found.[58] These results show that:

- partially reacted calcium or barium stabilizers (CaOORCl or BaOORCl) are stable and can exist in this form without converting into final chlorides,
- considering that PVC dehydrochlorination rate is not increased by the presence of these stabilizers (Figure 4.4), it is safe to conclude that these partially reacted with HCl products do not catalyze PVC dehydrochlorination.

The results of the above studies were neither confirmed nor rejected by more recent research. We may summarize properties of calcium, barium and the like, as follows:

- metal chlorides and partially reacted with HCl products do not catalyze dehydrochlorination,
- by reacting with HCl, these stabilizers eliminate its catalytic effect,
- there is no emission of HCl until they are not exhausted,
- products partially reacted with one HCl molecule are stable in the PVC environment and they undergo further reaction with HCl only after the first step of the above reactions was completed.

Cadmium and zinc chlorides

Figure 4.5 shows data obtained in a similar way as in Figure 4.4 but for zinc stearate. There is substantial difference between the two figures. In the case of calcium stearate experimental data form a linear relationship and their values are slightly lower than the values predicted from the equation. In Figure 4.5 experimental data follow a non-linear relationship and their values are lower than predicted from equation 4.2. There may only be one reason for this difference, namely that products of zinc stearate reaction with HCl have a catalytic influence on PVC dehydrochlorination rate. From the character of the experimental curve we may also conclude that this catalytic activity intensifies when concentration of stabilizer increases.

Numerous research works were published on the effect of reaction products of zinc and cadmium carboxylates on the PVC dehydrochlorination rate. Czako[59] found that reac-

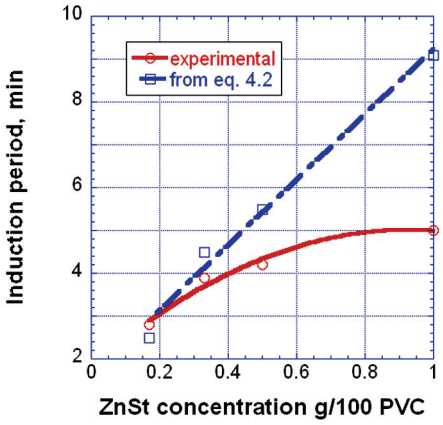


Figure 4.5. Induction period of PVC degradation vs. concentration of zinc stearate. [Data from Wypych, G., **Selected properties of PVC plastisols**, *Wroclaw Technical University Press*, 1977.]

tion of Cd stearate was a two-step reaction with partially reacted carboxylate (MeOORCl) formed in the first step and chloride ($MeCl_2$) in the next. Several other authors[60-65] made the same suggestions.

Several studies were performed by this author,[58] including elemental analysis and IR spectroscopy on samples of cadmium and zinc stearates reacted in moisture-free acetone with 50% of stoichiometric amount of HCl required to completely react with stabilizer. Elemental analysis of product of reaction showed that its concentration of carbon, hydrogen, oxygen, chlorine, and metal (either cadmium or zinc) was very similar to concentration of these elements in $ZnSt_2$ ($CdSt_2$) and very different than concentration of these elements in partially reacted zinc (or cadmium) stearates (MeOORCl).[58] Unlike in the case of calcium and barium stearates, IR spectrum did not show any additional peak which would indicate that only initial stearates were present.[58] This, in turn, suggests that these partially reacted stearates (MeOORCl) are not stable in this form and are rapidly converted to the final chlorides therefore only undetectable traces of partially reacted metal carboxylates (MeOORCl) are present in the mixture.[58]

It was suggested by this author that both the partially reacted stabilizer and the final chloride have catalytic activity towards PVC dehydrochlorination. Nagy[66] also mentioned the possibility that "hypothetical mixed chloride stearate" may catalyze initiation.

The effect of metal chlorides on degradation kinetics has been established in many papers.[50,65-79] Chlorides of aluminum, antimony, cadmium, and zinc accelerate the dehydrochlorination process, while others, especially those of barium and calcium, have no effect on the dehydrochlorination rate.

Vymazal[80] concluded that cadmium chloride may cause a rapid blackening and accelerate the dehydrochlorination rate of the sample only when cadmium chloride, stearic acid, and hydrogen chloride are simultaneously present in the polymer mixture. Their joint effect is attributed to the formation of coordination compounds by cadmium.

In connection with the mechanism of stabilizer action, Guyot[81] has remarked:

> If intermediate chloro-organozinc (or calcium) compounds are formed, we do not understand why they escape the coulometric titration which is carried out after dissolving the whole sample. If another unknown process destroys the chlorine formed through the substitution reaction, we do not understand why the process is not operative later.

Other doubts concerning the influence of reaction products come from Nagy:[66]

> We have to conclude that in cadmium-stabilized PVC the initiation of dehydrochlorination is faster than in absence of cadmium. This might be the effect of $CdCl_2$ but also the cadmium stearate or its hypothetical mixed chloride CdCl-stearate might catalyze initiation.

A few concepts have been put forward to explain the effect of metal salts on dehydrochlorination reaction. One concept includes complexing it with polyene sequences:[82,83]

$$ZnCl_2 + HCl \rightleftharpoons HZnCl_3$$

$$H_3C-CH=CH-CH=CH-CH_3 \xrightleftharpoons{HZnCl_3} H_3C-\dot{C}H-CH=CH-\overset{\oplus}{C}H-CH_3 \quad [HZnCl_3]^{\ominus}$$

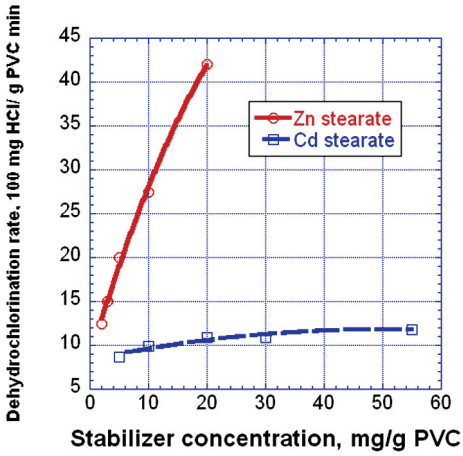


Figure 4.6. Effect of products of reaction of metal soap stabilizer on PVC dehydrochlorination rate. [Data from Wypych, J., *Polimery*, **20**, 38, 1975.]

Formation of the so-called polaron leads to increased dehydrochlorination rate. This information comes from electron spin resonance studies of model compounds (β-carotene),[82,83] The original observation and idea of complex formation between zinc chloride and polyenes came from Owen and Msayib,[84] who tried to cast films containing $ZnCl_2$ by evaporation of tetrahydrofuran solution at relatively low temperatures (65-90°C) and observed a change of color to blue-green. Owen and Msayib[84] adapted the mechanism of formation of Broensted acid from published studies on liquefaction of coal in which $ZnCl_2$ was used as a catalyst.

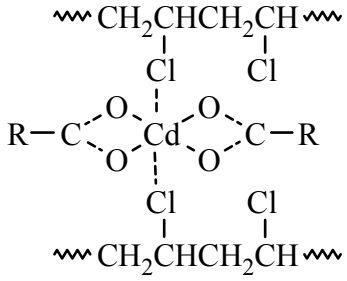
Figure 4.6 shows the relationships for cadmium and zinc stearates between their concentration and the dehydrochlorination rate after all stabilizer was consumed and dehydrochlorination rate became constant. Two observations can be made:[85]

- relationships are not linear,
- there is a substantial difference in catalytic activity of zinc and cadmium products of reaction with HCl.

It should be pointed out that if the concepts proposed by Tran *et al.*[82,83] and Owen and Msayib[84] were correct, the relationships should be linear because small additions of stabilizers are far below the number of available polyene sequences. Also, if the concept was universal there should be no such big discrepancy between behavior of cadmium and

zinc products of reaction. Gerrard *et al*.[86] were not able to repeat the experiment by Owen and Msayib.[84] They obtained similar spectra but of substantially different character.

Vymazal put forward a concept which is explained by the following chemical reaction scheme:[87]



Cadmium is known to form complexes having a coordination number of 6. The complex formed dissociates on a polymer side with subtraction of HCl molecule which remains associated with cadmium stabilizer. This model of reaction has substantial weakness:

- it assumes randomness of initiation,
- it implicates stabilizer in subtraction of HCl rather than its expected role of bringing stability to polymer,
- it bypasses a concept of defect structures which are considered responsible for initiation of dehydrochlorination.

In summary, the right principle was wrongly applied. It was postulated by this author in the previous edition of this book[88] that metal carboxylate has molecular symmetry which stabilizes formation of complexes as proposed by Vymazal but this may be affected by polar solvents affecting stability of partially reacted with HCl carboxylate. In the case of zinc carboxylate it is less relevant, considering that it is not very stable in PVC composition (see the above discussion).

Exchange of chlorine between different stabilizing forms is the most influential reaction for PVC stabilization and its mechanisms:[49,50,57,58,84,89-92]

$$ZnOORCl + CaOORCl \longrightarrow Zn(OOR)_2 + CaCl_2$$

$$ZnCl_2 + Ca(OOR)_2 \longrightarrow Zn(OOR)_2 + CaCl_2$$

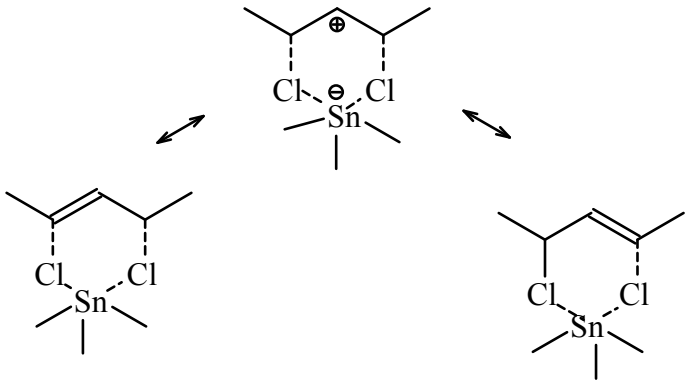
These two reactions and many other combinations of different reaction products or metals (e.g., Cd and Ba) constitute this mechanism aiming at lowering catalytic activity of metal salts. The principle is to keep a low concentration of chloride of metal which is capable of forming Lewis acids. The concentration of the zinc compound in the stabilizer form must be sufficient for the substitution of active chlorine atoms at a proper speed, but must not overcome the capacity of calcium stearate to convert zinc chloride into zinc stearate. This reaction forms one of the principles of stabilization and it will be further discussed in Chapter 11 in the section explaining mechanisms of PVC thermal stabilization.

Tin chlorides

Tin stabilizers react with HCl according to the following sequence:[93]

$$R_2SnY_2 \xrightarrow{HCl} R_2SnClY \xrightarrow{HCl} R_2SnCl_2 \xrightarrow{HCl} RSnCl_3 \xrightarrow{HCl} SnCl_4$$

Four chlorine-containing compounds can potentially be formed. These compounds differ in Lewis acidity. $SnCl_4$ and $RSnCl_3$ are strong Lewis acids and they affect dehydrochlorination rate similar to zinc and cadmium chloride.[22] Similar to zinc chloride, they cause catastrophic failure when they accumulate in sufficient concentration.[94] $RSnCl_3$ was even found to form green-blue compounds with polyenes in the same way as zinc chloride.[86] Lewis acidity also depends on the character of group R. For example, diphenyltin dichloride has higher Lewis acidity than dioctyltin dichloride because the phenyl group has electron withdrawing capability.[82] Dichlorides (R_2SnCl_2) should have theoretically lower stabilizing activity than monochlorides ($RSnCl_3$) from the point of view of Lewis acidity but they are better stabilizers because of formation of stabilizing coordination complexes as follows:[82]



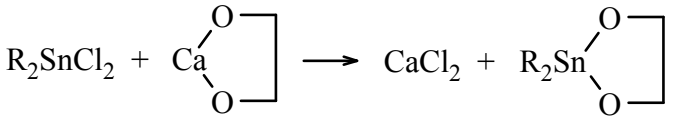
Chlorine exchange reaction is also central to the performance of tin stabilizers and their mechanism of action:[22,95-97]

$$R_2SnY_2 + R_2SnCl_2 \leftrightarrow 2R_2SnClY$$

$$2RSnY_3 + RSnCl_3 \leftrightarrow 3RSnClY_2$$

These and many other combinations of chlorine exchange reactions occur, which help to reduce catalytic activity of products of reaction with HCl.

Also, exchange reaction with calcium stabilizers occurs:[97]



Aluminum chloride

Catalytic dehydrochlorination of PVC occurs in the presence of aluminum chloride (1:1 molar ratio of PVC and $AlCl_3$), leading to completely dehydrochlorinated PVC – polyacetylene.[98] It should be noted that crosslinking occurs during this process. PVC heated with smaller concentrations of $AlCl_3$ (0.05 to 4%) dehydrochlorinates, forming shorter polyenes than without the presence of $AlCl_3$.[99]

4.1.3.2 Copper and its oxide

Studies were conducted to understand the processes of incineration of wire and cable which contain, in addition to PVC, copper, its oxide, and then chloride as a product of reaction with HCl.[100] Thermal degradation of PVC in the presence of copper and its compounds occurs at higher temperatures with major changes in the concentrations of the components of the gaseous products. These changes are caused by extensive crosslinking in the presence of copper and its oxide. Also, yields of aromatic hydrocarbons, such as benzene, are substantially decreased and yields of aliphatics are increased. Total chlorine emissions are reduced by 40% in air and 20% in nitrogen and benzene emissions are reduced by at least 90% in air and nitrogen.[100]

4.1.4 HYDROGEN CHLORIDE

In the early works on PVC dehydrochlorination, Arlman[101] ruled out the possibility of an autocatalytic effect of HCl on PVC degradation kinetics. Around the same time, other scientists came to the conclusion that only in an inert atmosphere does HCl not affect the dehydrochlorination process.[102-105] These early studies developed a lot of interest in HCl catalysis, and from the early sixties, after work done by Rieche,[106] it become evident that HCl plays an important role in the PVC degradation process. During this period an impressive account of HCl's autocatalytic effect was collected.[49,107-124] It is interesting to note a common agreement considering that it is not possible to obtain direct evidence that HCl actually causes increase in the dehydrochlorination rate because HCl is always present in unknown concentration in the reaction environment.

Endo and Emori[125] conducted an interesting experiment to determine influence of HCl on dehydrochlorination rate. Their dehydrochlorination experiments were conducted under a nitrogen blanket and in water heated under high pressure (19.6 MPa). In water, HCl was quickly dissolving and therefore it was removed faster from contact with PVC. Figure 4.7 shows that dehydrochlorination in water occurs with a reduced rate.

Figure 4.8 shows another experiment which compares dehydrochlorination rates with and without continuos removal of HCl. Degradation rate is faster if HCl is not removed. In addition, HCl was added in two different concentrations, causing an increase of degradation rate proportional to its concentration.[126] Other researchers conducted simi-

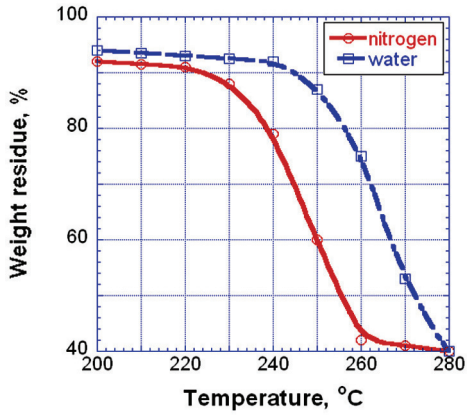


Figure 4.7. Dehydrochlorination of PVC sample for 30 min in water under high pressure (19.6 MPa) and under nitrogen blanket. [Adapted, by permission, from Endo, K.; Emori, N., *Polym. Deg. Stab.*, **74**, 1, 113-117, 2001.]

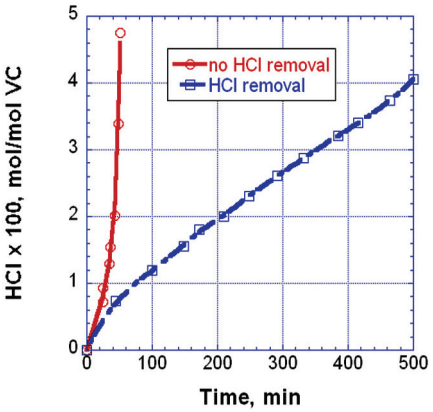
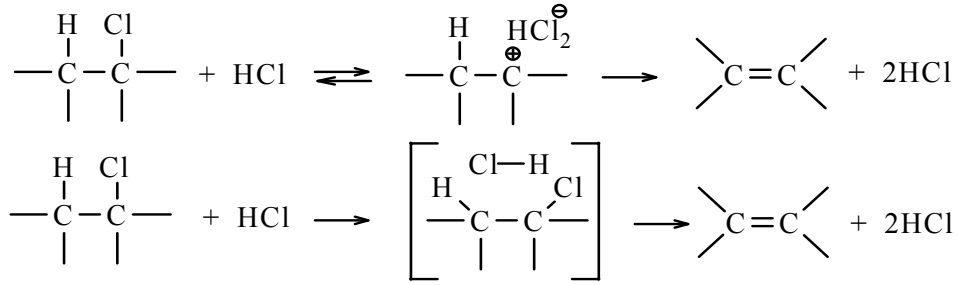


Figure 4.8. PVC dehydrochlorination at 200°C without removal of HCl (evacuated ampoules) and with continuous removal of HCl by freezing. [Data from Troitskii, B. B.; Troitskaya, L. S.; Yakhnov, A. S.; Novikova, M. A.; Denisova, V. N.; Cherkasov, V. K.; Bubnov, M. P., *Polym. Deg. Stab.*, **58**, 83-89, 1997.]

lar studies in which HCl was added into the stream of blanketing gas[127-129] or samples were exposed to HCl prior to degradation.[130] All these and other studies confirmed indirectly that HCl has an autocatalytic effect on PVC degradation.

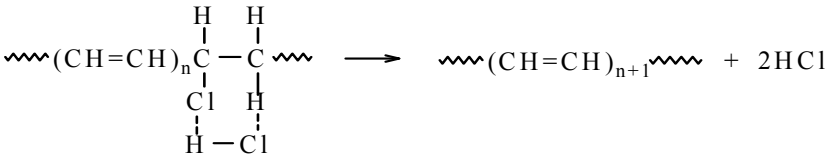
After these preliminary stages of studies, other questions became important, such as: How does HCl accelerate the process? What kind of mechanism is involved? Some questions remain unanswered, mainly due to the difficulties in measuring techniques.

Recent reviews contain suggestions regarding the mechanism of dehydrochlorination in HCl presence:[131,132]



The first is an ion-pair scheme and the concerted process is the second.[131,132] It is also suggested in these reviews that since PVC dehydrochlorination is enhanced in a similar magnitude as the model compounds by the presence of o-dichlorobenzene, this proves the mechanism is either ionic or quasi-ionic.[131,132]

An earlier comprehensive research paper reporting data on the influence of HCl on PVC dehydrochlorination gives a list of different mechanisms reported in literature. This list includes the above two mechanisms and one very important mechanism, as below:



It is important because it shows essential element – an act occurring in the vicinity of the double bond. Dehydrochlorination influenced by HCl certainly occurs when HCl is present, therefore there are double bonds already available in the chains which have undergone dehydrochlorination. The question now arises if the presence of double bonds enhances or retards the reaction rate of dehydrochlorination. Troitskii *et al*.[133] give the following dehydrochlorination rate constants:

~~CHClCH$_2$	7.4 x 10^{-8}
~~CH=CHCHClCH$_2$~~	4.0 x 10^{-4}
~~CH=CHCH=CHCHClCH$_2$~~	1.1 x 10^{-1}

This shows that regular segments degrade slower than allylic chlorines.

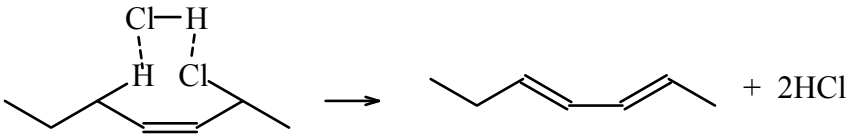
Autocatalytic dehydrochlorination reaction was modelled by quantum-chemical software, GAMESS.[134] This theoretical simulation compared regular segments of PVC chain with β-chloroallyl and polyenyl chloride groups. The following conclusions were drawn from the results of modelling:

- hydrogen chloride does not affect the rate of dehydrochlorination of regular units
- dehydrochlorination of regular segments occurs at the same rate with and without the presence of HCl
- hydrogen chloride catalyzes dehydrochlorination of β-chloroallyl and polyenyl chloride groups
- the most likely mechanism is by an exchange of atoms between HCl and an appropriate segment in PVC chain (see the mechanism given by Troitskii).[133]

This result does not come as surprise because it is well established that β-chloroallyl groups are labile structures formed in polymerization and they react first to initiate a chain of reaction. We[88] have previously reported based on MINDO calculations that polyenyl chloride groups assist propagation (this simulation will be further discussed below in the section of propagation reactions).

In order to fully discuss this mechanism of catalysis by HCl we have to go back to the section 4.1.1.3 of this chapter where *cis* and *trans* isomers are given. If we relate this

mechanism of chain extension and equation given by Troitskii, the mechanism of catalysis becomes clear and consistent with experimental data:



There should be very little doubt about this mechanism because it agrees with all underlining principles of PVC degradation which have been established by most researchers so far. These mechanisms are by no means recent discoveries. Ionic mechanism was proposed by van der Ven[113] in 1969, four-center HCl catalysis by Hjertberg and Sorvic[119] in 1978 and a mechanism similar to *cis* geometry by Morikawa[134] in 1968. These mechanisms were reported in the first edition of this book more than 30 years ago. It is important to mention it because it shows that many research works scrutinized these concepts and must have found them sound since they are still considered as valid.

The next question regards the influence of HCl from the point of view of physics. HCl has molar volume of 0.838 l/mol, molecular diameter of 0.322 nm, and an apparent activation energy of diffusion of 62.8 kJ/mol.[136] It is a small molecule easy to diffuse in any environment which does not preclude the fact that diffusion time depends on environment and tortuosity of pathways. Many authors claim "efficient" removal of HCl.[132] But with the most "efficient" removal there is always some time (no matter how small) which permits HCl to interact with sequences of chain according to the above equation. We know that metal soap stabilizers are very reactive and they are homogeneously dispersed in polymer, and this author has found that stabilizer presence reduces the catalytic effect of hydrogen chloride (see Figure 4.4).[49]

Real samples have three dimensions (for this purpose their thickness is the most important measure). Minsker[124] considered influence of sample size on the results of determination of dehydrochlorination rate and used samples of a thickness less than the critical one calculated from the following equation:

$$l_{cr} = \pi(D/k_3)^{0.5} \qquad [4.3]$$

where:

D	coefficient of diffusion,
k_3	effective constant of reaction catalyzed by HCl.

The problem is even more complicated than Minsker predicted.[124] If one combines his equation with Arrhenius' equation for constant k_3 and Gillands' equation for the diffusion coefficient, one obtains the following relationship after some parameters of the equations have been simplified:

$$l = CT^{0.75}e^{E/2RT} \qquad [4.4]$$

where:

T	temperature,
E,R	constants.

We can see, first of all, that the function is not complete. It has a minimum at T=2E/3R; therefore, a sample of thickness of l_{cr} would be affected by catalysis less than a sample of any other thickness, which does not offer stable conditions for measurement.

Early studies[137-139] revealed that when the electrical conductivity of samples is measured, the grain structure of PVC in the sample affects readings. Studies on PVC morphology[140-142] have demonstrated that PVC grain is built up from smaller particles causing formation of a free space inside the grains (see more in Chapter 3). Also, in suspension PVC the grain is surrounded by a sack-like skin, which contains microparticles and submicroparticles. One can easily imagine tortuosity of pathways complicating diffusion of HCl to the outside of the sample.

These structures are completely or partially destroyed during processing, therefore diffusion constantly changes. Different structures provide conditions for intermediate trapping of the HCl evolved. These problems remain unresolved both theoretically and experimentally and we do not know the magnitude of influence of HCl on dehydrochlorination rate because this must be related to the time of contact, which cannot be easily predicted in these complex geometries and influence of composition on the HCl diffusion rate.

Influence of HCl on polyene length was also a subject of studies. Owen[121] assumed that HCl catalysis may influence the distribution of polyene sequences during degradation and that it may also affect photochemical crosslinking reactions of polyenic cations. Braun[143] has done spectrophotometric studies in order to compare the length of polyene sequences when PVC samples in the form of powder and film were degraded. In the case of PVC powder, he found that the higher the temperature, the shorter the polyenes, whereas PVC in the form of a film exhibited just the opposite relationship. Thus, the form of a sample may influence the result, and finally, the conclusions. There is now general agreement that HCl presence increases polyene length.[3,144,145]

There are a few additional observations regarding this topic. Chlorinated PVC is more stable because double bonds were saturated with chlorine during the chlorination process.[146] Some authors believe that polyenes can be shortened by HCl readdition into polyene sequence.[147] Entropy of PVC dehydrochlorination reaction is lower than entropy of model compounds because of the influence of HCl autocatalysis.[3] It was calculated that it will take 2 billion years for PVC to lose 1% chlorine at 40°C.[148]

4.1.5 IMPURITIES

Many research papers mention impurities but do not identify their composition and the way in which they may interfere with thermal degradation. Some impurities were found to be introduced with additives, such as fillers,[149,150] plasticizers,[151] and solvents (most likely in the case of sample preparation but sometimes they are introduced with additives).[152] There is no information in these papers on how these impurities may influence thermal degradation. It was pointed out that polymerization impurities do not seem to interfere with thermal stability of polymer because it does not change after reprecipitation.[36]

The only documented dangers of influencing thermal stability of PVC are reported in works on recycling.[31,153-155] The most frequent impurities include polymers (e.g., PET and PE),[31] paint and ink residues, glue residues, metal traces, and contact media.[154,155] This

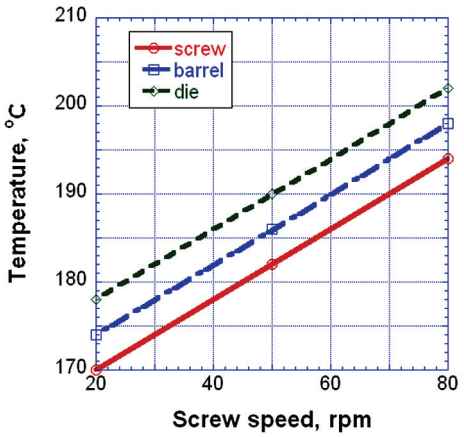


Figure 4.9. Screw speed vs. extrusion temperatures. [Data from Covas, J. A.; Gilbert, M., *Polym. Eng. Sci*., **32**, 11, 743-750, 1992.]

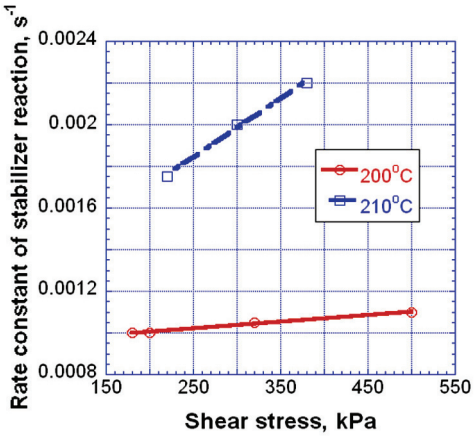


Figure 4.10. Rate constant of stabilizer reaction vs.shear stress for PVC siding capstock compound at two different temperatures. [Data from Bacaloglu, R.; Fisch, M.; Steven, U.; Bacaloglu, I.; Krainer, E., *J. Vinyl Additive Technol.*, **8**, 3, 180-193, 2002.]

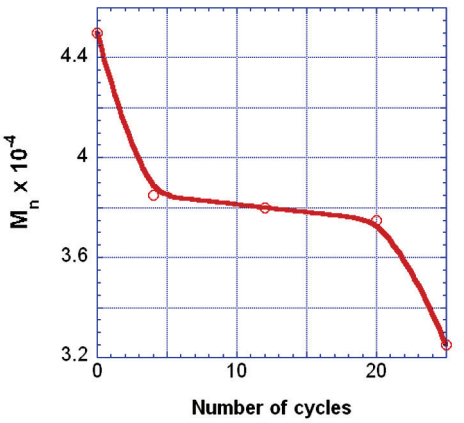


Figure 4.11. Number of jet milling cycles vs. molecular weight of PVC. [Data from Xu, X.; Guo, S.; Wang, Z., *J. Appl. Polym. Sci.*, **64**, 12, 2273-2281, 1997.]

type of contamination poses danger to polymer stability as well as to retention of mechanical properties and esthetic values.

4.1.6 SHEAR

Shear increases temperature of melt (Figure 4.9).[156] It is usually difficult to the separate effect of shear and heating on temperature but capillary rheometry permits their separation.[16] Figure 4.10 shows rate constants of stabilizer reaction with PVC degradation product as a function of shear stress and temperature.[16] Increase in temperature and shear stress increases stabilizer consumption (and dehydrochlorination rate).[16] This information shows that stationary testing of thermal degradation does not include all influences and a correction must be introduced to account for the effect of shear on temperature increase.

It was demonstrated (Figure 4.11) that jet milling affects molecular weight of PVC.[157] Also its molecular weight distribution is affected.

In injection molding process, rate of material flow and its distance from the wall influence temperature.[158] If conditions of flow are too severe, temperature rises above critical for thermal stability of material and injection molded parts show shear burning.[158,159]

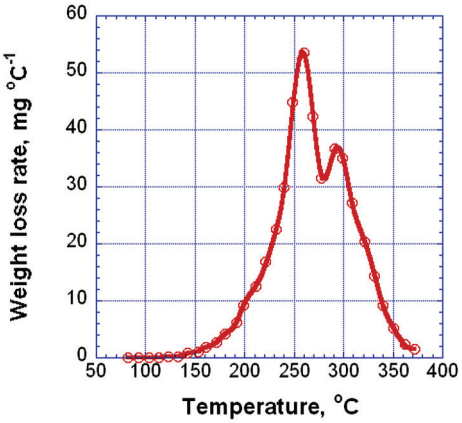


Figure 4.12. Thermogravimetric curve of PVC degradation. [Adapted, by permission, from Jimenez, A.; Iannoni, A.; Torre, L.; Kenny, J. M., *J. Thermal Anal. Calorimetry*, **61**, 2, 483-491, 2000.]

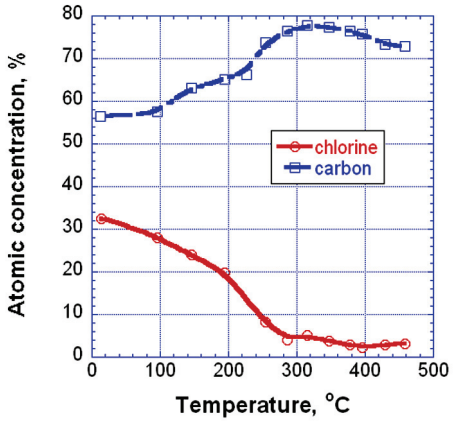


Figure 4.13. Concentration of elements in degradation of PVC without additives in air as a function of temperature. [Data from Dumitrascu, N.; Borcia, G.; Popa, G., *J. Appl. Polym. Sci*., **81**, 2419-2425, 2001.]

Shear burning resistance of material can be increased by selection of polymer (more stable or lower viscosity) or stabilizing package.

The above examples show that shear may influence thermal performance of PVC in many processes. The most extensive influence is observed in extrusion and many molding processes which require high shear rates.

4.1.7 TEMPERATURE

Temperature is obviously the most important parameter of thermal degradation. In this context we may only consider data describing changes in chemical composition but it will be more appropriate to also present data on other properties which lead to deterioration of properties of PVC materials. We will illustrate the effect of temperature by a selection of experimental data.

Figure 4.12 shows the effect of temperature on weight loss. Two curves are overlapped.[160] The first curve gives data on plasticizer evaporation and the second on thermal degradation of PVC. The second curve mostly reflects HCl loss but also formation of some aromatic content. Figure 4.13 characterizes formation of two components (HCl and aromatics).[161] Two phases can be distinguished: until about 350°C the concentration of carbon increases because of gradual loss of chlorine; above 350°C also, carbon concentration decreases because degraded polymer becomes oxidized and volatile products are produced from carbon.[161] The last two figures also show that thermogravimetric analysis gives data difficult to interpret because of the influence of additives and oxidation.

Figure 4.14 shows rate constant of HCl evolution vs. temperature. With increased energy, the rate constant increases rapidly.[6,14] Figure 4.15 shows time required to emission of 1% HCl. For the graph's clarity, the value for 40°C was omitted which is between 0.4 to 2 billion years.[163] Figure 4.16 shows plasticizer loss at relatively low temperatures during 2 hours of exposure of PVC containing dioctyl phthalate and benzyl butyl phthalate

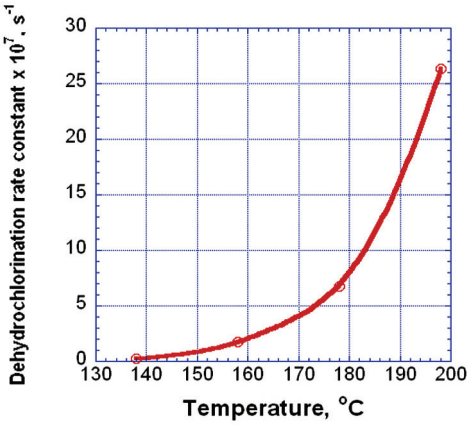


Figure 4.14. Dehydrochlorination rate constant vs. temperature. [Data from Fisch, M. H.; Bacaloglu, R., *J. Vinyl Additive Technol.*, **1**, 4, 233-40, 1995.]

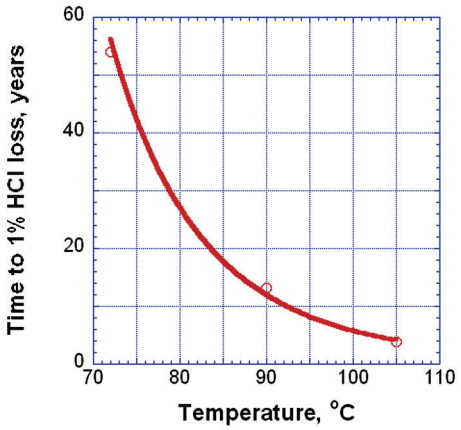


Figure 4.15. Time to 1% dehydrochlorination vs. temperature. [Data from Hitt, D. J.; Gilbert, M., *J. Appl. Polym. Sci.*, **89**, 14, 3859-3867, 2003.]

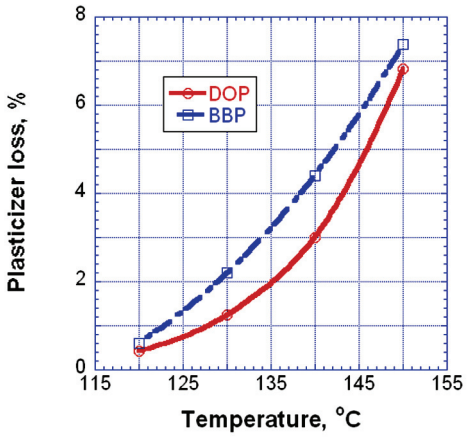


Figure 4.16. Plasticizer loss vs. temperature. [Data from Mrklic, Z.; Kovacic, T., *Thermochim. Acta*, **322**, 2, 129-135, 1998 and **414**, 2, 167-175, 2004.]

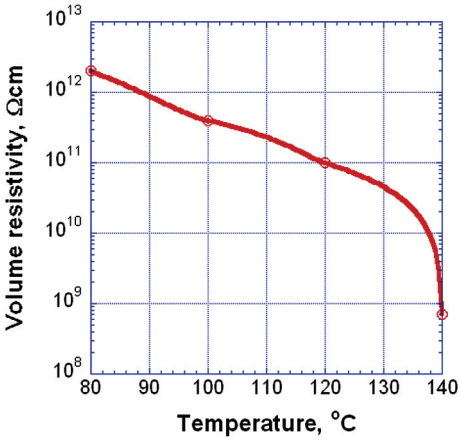


Figure 4.17. Volume resistivity change after aging plasticized PVC for 1000 h at different temperatures. [Data from Nedjar, M.; Beroual, A.; Boubakeur, A., *J. Appl. Polym. Sci.*, **102**, 5, 4728-4733, 2006.]

(PVC:plasticizer=2:1).[166,167] It is pertinent that retention of low molecular plasticizers is limited at elevated temperatures.[165]

Electrical properties are also affected by temperature (Figure 4.17). Volume resistivity decreases (more rapidly above 120°C) and dielectric loss factor and dielectric constant increase (also rapid increase is observed above 120°C).[168]

Temperature affects mechanical properties of PVC materials, such as fatigue, tensile, or hardness, and even surface roughness increases with increasing temperature.[169]

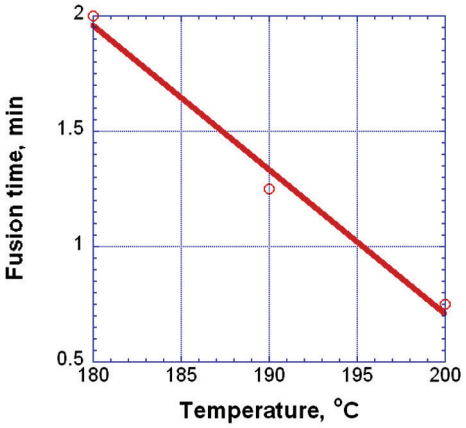


Figure 4.18. Fusion time vs. temperature. [Data from Chen, C.-H.; Mao, C.-F.; Lo, Y.-W., *J. Appl. Polym. Sci.*, **81**, 12, 3022-3029, 2001.]

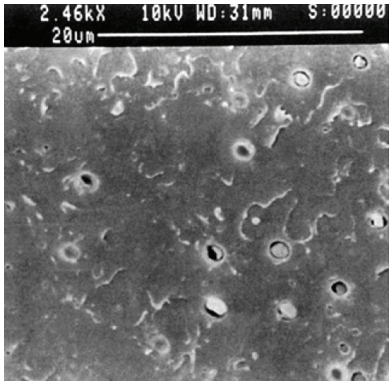


Figure 4.20. SEM of PVC processed at 200°C. [Adapted, by permission, from Comeaux, E. J.; Chen, C. H.; Collier, J. R.; Wesson, R. D., *Polym. Bull.*, **33**, 6, 701-8, 1994.]

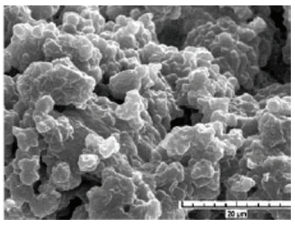


Figure 4.19. Suspension PVC after processing in Brabender chamber to minimum torque at 160°C and 17.38 s^{-1}. [Adapted, by permission from Tomaszewska, J.; Sterzynski, T.; Piszczek, K., *J. Appl. Polym. Sci.*, **93**, 2, 966-971, 2004.]

All the above examples show vulnerabilities of PVC materials in applications which require elevated temperatures during processing. There is an important reason for thermal treatment, namely fusion or gelation. Because of unusual morphology, PVC relies heavily on formation of crystallites and entanglements. The mechanisms of fusion and gelation depend on the method of processing and their discussion goes beyond the scope of this book. Figure 4.18 shows that fusion time decreases with temperature increase.[170] The goal of fusion and gelation processes is to obtain a homogeneous mixture of components. The more homogeneous the material, the better the mechanical performance, although mechanical performance also depends on formation of crystalline structure on cooling. From the previous chapter it is known that PVC grains have complex morphology (especially suspension PVC). The goal of fusion is to destroy this structure which can only be accomplished by use of elevated temperature and shear. Figure 4.19 shows results of PVC compounding until minimum torque is reached in a Brabender plastograph.[171] At this point of compounding, the primary grains are mostly disintegrated into particles with average dimensions between 4 and 20 μm. The dimensions of the particles created in this way correspond generally to the dimensions of agglomerated primary particles. Particle integrity is still retained and free spaces are clearly visible. On further compounding, torque increases and particles are fused together without clear boundaries (Figure 4.20).[172] At higher processing temperatures, interfusion between PVC microparticles caused the formation of a tri-dimensional network. At lower

temperatures, such as 160°C, this tridimensional network is very poor and discontinuous, which affects mechanical properties.

4.1.8 SURROUNDING ATMOSPHERE

Although PVC is usually processed under normal atmospheric conditions, most studies are conducted in an inert atmosphere. Because of the multiplicity of factors affecting the thermal degradation of PVC, there is great concern to limit them to the necessary minimum. Studies conducted in the presence of inert gases serve as a point of reference.

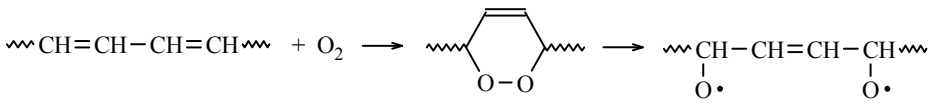
The dehydrochlorination rate is believed to be linearly dependent on temperature, as demonstrated by the Arrhenius plot.[173,174] The activation energy reported is in the range of 30 to 160 kJ/mol. PVC degradation in an inert atmosphere has the following predominant features:

- initiation of the process of dehydrochlorination by labile structures in the polymer chain,
- dehydrochlorination with two simultaneous reactions occurring, polyene structure formation and crosslinking,
- the molecular weight of the initial polymer is affected by the crosslinking process; chain scission is not a typical feature of this process,
- color formation results from at least two competitive factors, polyene length distribution and the concentration of crosslinks.

Fewer studies have been done on PVC degradation in the presence of oxygen than in an inert atmosphere. Let us begin our discussion by first pointing out some differences between the two processes. The dehydrochlorination rate in pure oxygen is perhaps two to five times larger than in inert gas.[175] Some authors[176,177] have found the increase in the dehydrochlorination rate to be proportional to the square root of the oxygen partial pressure. The increased rate of dehydrochlorination might be explained by the formation of new initiation centers because of oxidation. Gupta[178] demonstrated that the introduction of oxygen during the thermal degradation of PVC in inert gas immediately changes the rate of dehydrochlorination.

Initiation of thermal degradation is thought to be the same in both cases.[179] The activation energy of dehydrochlorination in oxygen is around 125 kJ/mol,[179] which means it is in the same range as in inert gas.

A difference can be noticed on the propagation stage, as there are two competing reactions in the presence of oxygen, zip-like dehydrochlorination and oxidation of already-formed double bonds. Practical consequences are easily observed, as discoloration proceeds more slowly than in an inert atmosphere.[180,181] The oxidation of longer polyenes is thought to be faster than that of shorter ones.[182] The reaction mechanism proposed by Druesdorf:[183]



includes the possibility of the creation of radicals, which are thought to increase the dehydrochlorination rate.[178]

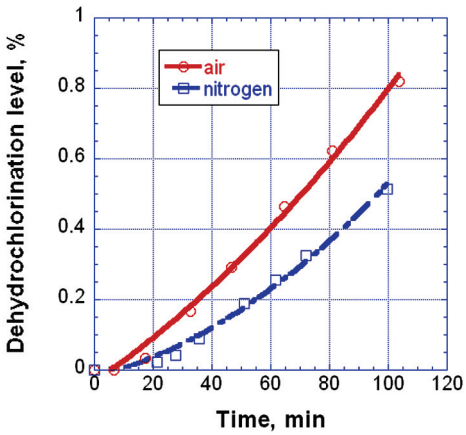


Figure 4.21. Dehydrochlorination of PVC in air and nitrogen. [Data from Hillemans, J. P. H. M.; Colemonts, C. M. C. J.; Meier, R. J.; Kip, B. J., *Polym. Deg. Stab.*, **42**, 3, 323-33, 1993.]

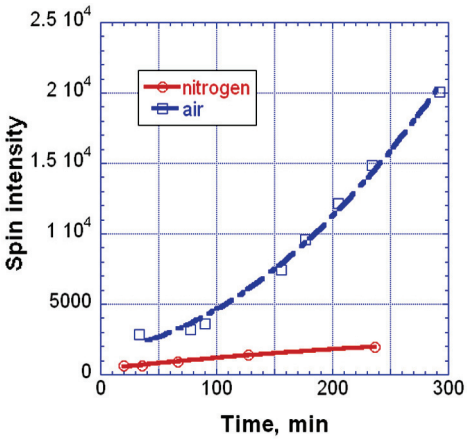


Figure 4.22. Spin intensity vs. heating time at 180°C under nitrogen and air. [Data from Nguyen, T. P.; Lefrant, S.; Tran, V. H.; Guyot, A.; Molinie, P., *Synthetic Metals*, **51**, 277-283, 1992.]

The molecular weight is affected during thermooxidative processes by both crosslinking reactions and chain scissions.[178,184,185]

According to Gupta,[178] crosslinking started in the presence of oxygen after three hours of degradation at 463K, while in inert gas, the sample already contained 53% crosslinked material. Weight loss under oxygen was 2.1 to 3.7 times faster than under nitrogen.[186]

Figure 4.21 compares rates of HCl emitted under air and nitrogen.[187] Test results are available[188] for temperatures from 150 to 180°C and dehydrochlorination rate under nitrogen is always substantially slower than under air. Figure 4.22 shows that larger number of π-electron systems are formed under air than nitrogen.[188]

4.1.9 ELECTRICAL BREAKDOWN (SPACE CHARGE FORMATION)

An exothermic reaction reaching temperatures above 150°C can be caused by overload currents or inferior electrical wire connections.[189] This may cause deterioration of insulating properties in PVC due to its chemical decomposition.[189] The heat treatment above 150°C degrades the breakdown properties of PVC cables working in temperatures from room temperature to 90°C due to previous thermal decomposition accompanied by dehydrochlorination of PVC.[189] Electrical conductivity of PVC can acquire an anomalous character due to aging.[190] Transition of PVC from a state with usual (low) conductivity into a state with anomalously high conductivity was observed.[190]

4.1.10 ADDITIVES

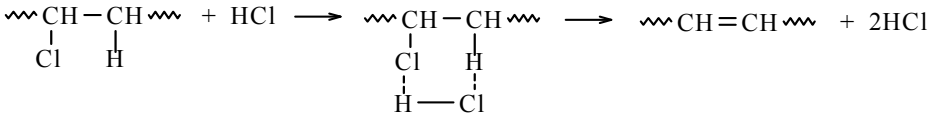
Additives are always present in PVC to modify its properties. They also usually modify its thermal stability. The last section of this chapter is devoted to the analysis of the influence on thermal stability of property improving additives.

4.2 MECHANISMS OF THERMAL DEGRADATION

PVC degradation is a complex process difficult to describe as a mechanism which considers all its aspects. Some known mechanisms represent only one process, others a sequence of several steps. The types of description include chemical reactions, physical state of molecules, kinetics, or thermodynamics. Below we review the most important chemical mechanism of PVC thermal degradation in the hope that they may jointly help to bring us closer to a more comprehensive description of the mechanism of PVC thermal degradation.

4.2.1 MOLECULAR MECHANISM

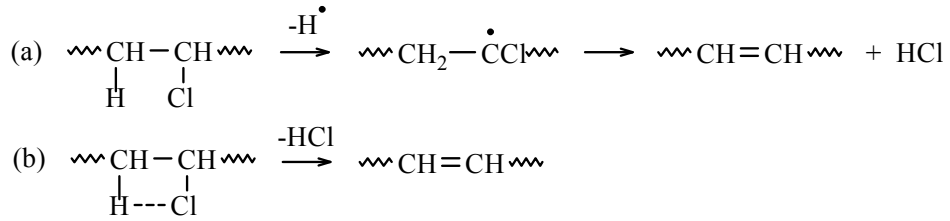
Molecular mechanism predicts initiation of autocatalytic degradation by interaction between HCl and regular units of chain according to the following reaction:



This mechanism does not include formation of radical or ionized groups; therefore there is no chain transfer but each act of HCl split off is a separate act. This mechanism will contradict the influence of labile centers, extension of conjugation, and particularly, formation of long polyenes by propagation of chain reactions.

4.2.2 AMER-SHAPIRO MECHANISM

Amer and Shapiro[122] did not find a large difference between activation energy for HCl catalyzed dehydrochlorination and for uncatalyzed dehydrochlorination. They proposed a three-step mechanism which rationalizes their data. The first step is a generation of a *cis* double bond:[122]



Two mechanisms are allowed: (a) radical or (b) 1,2-unimolecular elimination.[191] Step one is considered a slow, rate-controlling reaction. In the case of radical process the likely site of this initiation reaction is that of some labile group. Only macromolecular radicals in which the β-hydrogen is abstracted are capable of supporting the chain process.

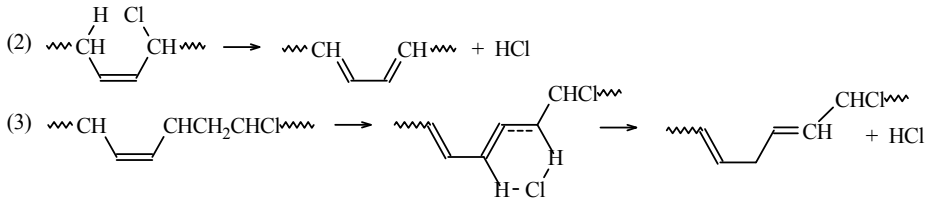
If unimolecular reaction is considered it eliminates labile groups from initiation of dehydrochlorination. If radical process is considered, then it more likely happens on exposure to radiative processes or mechanochemical degradation.

It is important to stress that the first step is expected to form *cis* double bond for reaction to proceed further in steps 2 and 3. This is an important suggestion put forward by Amer and Shapiro.[122]

The next two steps are part of another mechanism which is called a six-center concerted mechanism and it is discussed in the next section.

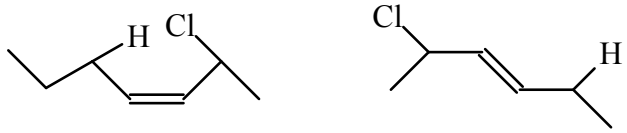
4.2.3 SIX-CENTER CONCERTED MECHANISM

Amer and Shapiro proposed the following two steps in their three-step mechanism (see the first step in the previous section):[122]



The second step consists of six-center elimination of HCl. The second step accounts for HCl catalyzed double bond shift. The repetition of steps is expected to continue as long as syndiotactic conformation is retained by the section of chain.[122]

Bacaloglu and Fisch[3,4] used molecular orbital calculations[3] and correlation[4] of activation entropies and enthalpies for dehydrochlorination of chloroalkanes, chloroalkenes, and PVC to verify elements of Amer's and Shapiro's mechanism (see more on this subject in the next section). They came to the conclusion that the concerted six-center reaction agrees with their findings but they have modified the 3rd step of Amer's and Shapiro's mechanism[122] to account for propagation and termination steps. This has resulted in a simple explanation of why polyenes continue to grow or stop growing:



cis reactive **trans stable**

In *cis* configuration, hydrogen and chlorine atoms may participate again in six-center elimination and follow the pattern of zipping reaction. This is restricted by *trans* configuration where potentially reactive groups are too distant to react.

In the author's[3,4] own words, the mechanism operates as follows: "The six-center allylic 1,4-eliminations from polyenes are preceded by a 1,3-rearrangement of a hydrogen atom that generates the *cis* or *trans* allylic system from the conjugated polyene in an equilibrium. This process is catalyzed by hydrogen chloride present at the reaction site because of the formation of a π-complex with the system of double bonds. If hydrogen chloride diffuses away from the reacting center before the 1,3-rearrangement takes place, the chain elimination is interrupted. As long as the hydrogen chloride is present, *cis* and *trans* allyl chlorides equilibrate with conjugated polyenes and *cis* allyl chloride eliminates quickly.

As soon as HCl has left the reaction site, the *trans* isolated allylic chloride or the conjugated polyene becomes stable and the elimination process stops."

The above mechanism forms very elegant and consistent sequence of events describing results of many studies. The major weak point is in the lack of justification and data confirming 1,3-rearrangement which is crucial for the continuity of zipping reactions. This mechanism, similar to many other commented in this chapter did not escape strong criticism[26,191] (see discussion in the next section).

4.2.4 ACTIVATION ENTHALPY

Bacaloglu and Fisch[4] gathered a large number of activation enthalpies and entropies data for dehydrohalogenation of allylic chloroalkenes, tertiary chloroalkanes, and secondary chloroalkanes in the gas phase available in literature from 1938 to 1993. They found that activation entropies and enthalpies give relatively good correlation in spite of the fact that data were obtained in different solvents. Enthalpy-entropy correlations for the experimental data available on dehydrochlorination of chloroalkanes and chloroalkenes show that these reactions in the gas or the liquid phases in non-polar solvents are molecular processes. Bacaloglu and Fisch[4] concluded that dehydrochlorination is a molecular reaction catalyzed by HCl.

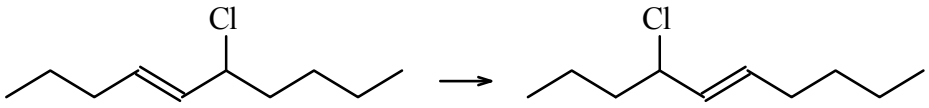
Elimination of HCl from allylic chlorine (chain propagation) was found to require much less energy (~52 kJ/mol) compared with formation of double bond in the initiation process (~135 kJ/mol). Also, formation of *trans* polyene (chain interruption) was energetically less favored (~78 kJ/mol) than formation of *cis* polyene (propagation) (~52 kJ/mol). Based on these data, Bacaloglu and Fisch[4] postulated a framework of the modified Amer and Shapiro[122] mechanism of dehydrochlorination. They have included both tertiary chlorines and allylic chlorines as potential initiating sites with allylic chlorines favored due to their lower activation energy. It should also to be noticed from these studies that the activation enthalpy of condensation of conjugated polyenes to benzene was found to be very low (~30 kJ/mol).[4]

A semiempirical MNDO procedure with parametrization (AM1) was used to calculate energies, geometries, charges and spin densities.[3] The results of these calculations supported molecular mechanism of PVC dehydrochlorination. It was further discovered that under certain conditions, radical and ionic mechanisms were also possible. These special conditions for ionic mechanism include dehydrochlorination in highly polar solvents and explain catalytic effects in the presence of Lewis acids (e.g., $ZnCl_2$, $CdCl_2$, and $SnCl_4$).[3] The special conditions for radical mechanism of degradation included reactions in the presence of high energy radiation, oxygen, impurities, and overheated regions of PVC.[3] All these special conditions do not seem controversial, with the exception of broadly defined "overheated regions".

The degradation mechanism of PVC presented by Bacaloglu and Fisch was fiercely criticized by Starnes and his group ("Any stabilization technology that requires the operation of the new six-center mechanism should be regarded skeptically, and it certainly should not be considered seriously for use in commercial products"[132] and "Six-Center Concerted Mechanism for Poly(vinyl chloride) Dehydrochlorination. Requiescat in Pace?"[188]). Starnes *et al.*[191] showed that dehydrochlorination of the allylic chloride, 5-

chloro-6-decene is much faster than the dehydrochlorination of 4-chloro-6-tridecene. This will indicate that the isomerization of 4-chloro-6-tridecene into an allylic chloride by 1,3-hydrogen rearrangement is a much slower process than the elimination itself. Bacaloglu and Fisch adapted the 1,3-rearrangement of hydrogen from the mechanism presented by Amer and Shapiro[122] to explain the formation of the *cis*-allylic active intermediate from *trans,trans* dienes and polyenes.

Starnes *et al*.[191] also show that the 1,3-rearrangement of chlorine on the heating of 5-chloro-6-decene is quite a fast reaction, faster than dehydrochlorination:



Perhaps this or some other reaction may explain the mechanism of 1,3-rearrangement. But studies are required to produce data which will be able to confirm any theoretical prediction of the sequence of events. It also should be taken into consideration that Starnes *et al.*[191] data come from a single model compound (not PVC) and may not be fully applicable to explain behavior of the polymer chain. At this point the proposed mechanism is still attractive but incomplete.

4.2.5 RADICAL-CHAIN THEORY

From the previous sections we can list potential applications of radical theory which explain the observed data:

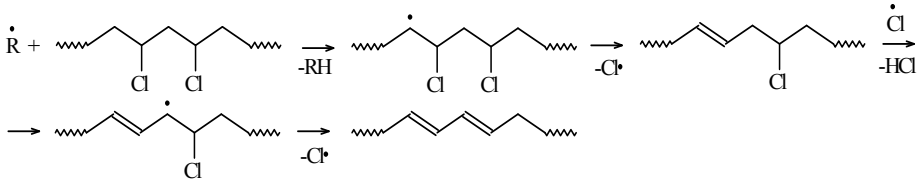
- high energy radiation,
- impurities,
- oxygen presence.[195]

The last two may occur during thermal degradation.

Existing literature gives some examples of processes which can be explained by radical theory. They include:

- degradation in the presence of catalyst residue,[22]
- the presence of transfer catalyst,[192]
- benzene formation,[33]
- crosslinking[193] and chain scission,[22]
- incineration.[194]

Winkler[196] was the first to propose a radical mechanism in 1959, as follows:



In the case of his studies the initiating radical was provided by the catalyst residues. We can see from the scheme that once the radical process begins, it continues extending

polyenes. Similar influence and mechanism is believed to take place during dehydrochlorination in the presence of phase transfer catalyst (tetrabutyl ammonium bromide).[192]

Benzene formation begins at low temperatures (slightly above the glass transition temperature) as soon as polyenes of suitable length are available. This process has been observed at a very low degree of dehydrochlorination (0.5% at 180°C).[33] Several mechanisms for benzene formation have been proposed, including the cyclization of a triene radical situated at a chain end and the Diels-Alder condensation.

Crosslinking[193] and chain scission[22] are reported for dehydrochlorination under nitrogen and air (see prior discussion in this chapter). The presence of oxygen also was found to accelerate the process due to formation of free radicals.[193,195] Molecular weight studies give clear evidence of these processes. None of the mechanisms presented so far can be used to explain these two processes and, in fact, it is difficult to imagine any other explanation than one based on radical processes.

Electron spin resonance spectroscopy helps to measure paramagnetic centers. Origin of some of these centers found during thermal degradation is identified and linked to alkyl radicals and polyenyl radicals, but the chemical structure of some paramagnetic centers in PVC are not known. [197] Stable polyenyl radicals are known to exist in thermally degraded PVC.[197] In addition to the need to explain some observed changes (e.g., crosslinking and chain scission), it is therefore certain from ESR studies that radical processes do occur during thermal degradation.

PVC pyrolysis occurs according to a liquid phase chain radical mechanism at temperatures higher than 200°C.[194] Several mechanisms and various simplified models are discussed in literature. The researchers agree on the presence of two: initial dehydrochlorination forms HCl and polyene structures. During this phase, benzene and some naphthalene and phenanthrene are also formed through Diels-Alder reactions and successive dealkylation of polyene molecules. After chlorine has been quantitatively released from the melt, the polyene molecules rearrange and, through cyclization and crosslinking reactions, form alkyl aromatic hydrocarbons and char residues.[194]

Starnes[132] analyzed radical thermodegradation and put forward several observations placing limits on radical degradation:

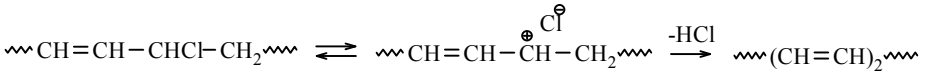
- model compound (*trans*-4-chloro-5-decene) heated at 180°C in toluene did not produce any reaction products with toluene,
- energy of homolytic dissociation of aliphatic C-Cl bonds is higher than the energy of thermal dehydrochlorination in condensed phase.

Starnes[132] proposed that radical processes in thermal degradation are responsible for transfer process that generates new labile defects and leads to autoacceleration.

4.2.6 IONIC

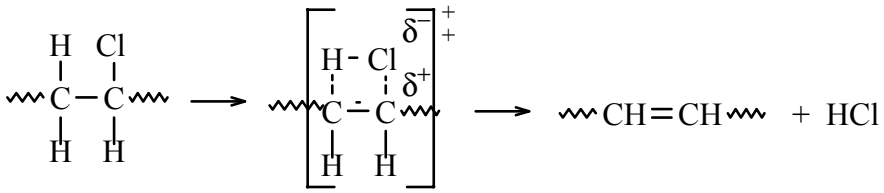
It is surprising that the ionic mechanism of degradation mentioned in almost every paper on PVC thermal degradation has such a small amount of credible research work in which its features, advantages and disadvantages are discussed. Starnes[132] has been the most fre-

quent advocate of this mechanism, and his ion-pair mechanism is given by the following equation:



The ion-pair mechanism simply shows that an ion pair formed in α-position to the double bond is the first act of extension of sequence of conjugated double bonds. Every next step follows the same pattern.

The so-called quasi-ionic mechanism is given by the following equation:



The catalysis of dehydrochlorination is accounted for by an ion pair with HCl_2^- ion or the concerted process.[132]

There is no explanation regarding termination or propagation of polyene sequences except for molecular calculations made by Haddon and Starnes[198] and Wypych and Stepien[88] which were later criticized by Meier and Kip,[199] who rejected the proposed idea of a termination caused by the effect of polyene length on activation energy (see full discussion of this subject below in Section 4.3.3).

Ionic mechanism does not explain the effect of oxygen on increased rate of dehydrochlorination.[200] Comprehensive kinetical analysis of different mechanisms by Troitskii and Troitskaya[201] shows that predicted kinetical data from a model based on ionic mechanism do not agree with experiment.

Most of the supportive data for this mechanism is based on low molecular weight models and many critical points still require research.[132]

4.2.7 POLARON

A group of French scientists proposed a polaron mechanism, details of which can be found in their papers.[56,81-83,188,200,202-207] Papers contain description of the mechanism,[83,200] explanation of used terminology,[200,202] and data which justify various steps and applications of the polaron mechanism.[56,81-83,188,200,202-207]

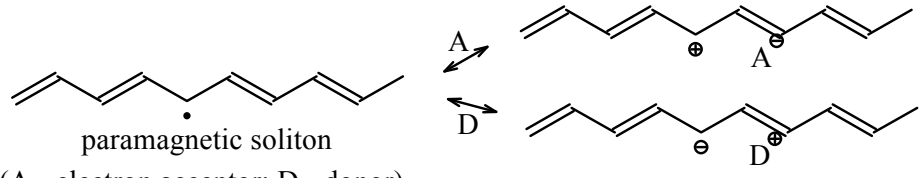
Several concepts of physics are used in the description of "the polaron mechanism"; their meaning is as follows:

- polaron is a π-radical-ion; a radical cation that is partially delocalized over several polymer segments is called a polaron. The name is devised from the fact that it stabilizes itself by polarizing the medium around it. It is paramagnetic and its density depends on the concentration of the oxidoreduction agent or dopant,
- soliton is a π-radical easily formed in *trans-transoid* polyacetylene; it is considered to be able to move almost freely along the chain in the same way as a solitary wave – hence the name "soliton"; solitons have no charge but a spin of 1/2,

therefore solitons are paramagnetic; the population of solitons is low – approximately 1 per 1000-3000 VCM,[83]

- bipolaron is π-di-ion; with high dopant concentration, the polaron becomes a bipolaron or di-ion (diamagnetic) or after further interaction of another dopant with its neutral soliton,
- exciton is an energy state caused by π-orbital phase changes due to structural isomerization by interchange of adjacent single and double bond.

Structural formulas of polaron, soliton, and bipolaron (di-ion) are as follows:



paramagnetic soliton
(A - electron acceptor; D - donor)

diamagnetic charged soliton

polaron

positive bipolaron (di-ion)

Polaron mechanism is an alternative mechanism to ionic and radical mechanisms. It can account for features of the two mechanisms, as follows:

- soliton or charged soliton deactivates the allylic chlorine atom by reducing electron density of the chlorine atom at α-position to double bond
- solitons or charged solitons accelerate the degradation, because the methylene hydrogen atoms adjacent to them become activated due to the electronic deficiency in the σ-bond (C-H*)
- the neutral solitons of the polaron either combine with each other or are oxidized by the Lewis acid compounds (e.g., chlorides of reacted stabilizers) to form diamagnetic bipolarons. It is also possible that the Lewis acid compounds cause further degradation of the PVC by catalyzing re-addition of HCl to double bonds,[82,203]
- the solvents (or other additives), by their doping or redox power, create, with π-electrons of the double bonds in PVC, polarons, which lead to dehydrochlorination; the more powerful the redox properties of a solvent, the higher the dehydrochlorination rate and the longer the *trans* polyenes sequences and the more important the influence of the crosslinking reaction,[83]
- the mechanisms of stabilization by organotin compounds are controlled by the state of the π-electrons in the double bonds of degrading PVC,[204]
- oxygen (electron acceptor) first oxidizes a double bond to form a polaron, hence catalyzed chain degradation occurs,[188,200]

- any electron withdrawer should behave in exactly the same way: it should cause the oxidation of the double bonds to build up polarons. This accounts for the degradation, regardless of the nature of the catalyst.[200]

The above list of features shows that the polaron mechanism is the most comprehensive out of the already discussed mechanisms. It accounts for initiation by allylic and tertiary carbon chlorides, propagation,[208] effect of oxygen, effect of catalytic influences, effect of chlorides from metal carboxylate and tin stabilizers, and helps to explain stabilization.

Critics dispute the following problems with the mechanism:

- extension of polyenes does not have a mechanism of termination, therefore polyenes will grow indefinitely,[209]
- stabilization by the replacement of an allylic methylene hydrogen with an organotin functionality that is attached to the polymer by a stable C–Sn bond,[132]
- it does not address the question of autocatalysis[191] (this is incorrect, as seen from the above features of the polaron mechanism)
- limited experimental evidence.[132]

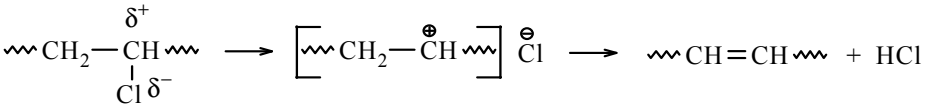
Formation of paramagnetic species in the course of thermal degradation is very well proven by electron spin resonance studies.[133,202-207] Also, many experimental results of application studies were presented by the authors of polaron mechanisms. Studies done on PVC included thermal degradation and thermal stabilization. It should be mentioned that studies are performed in solvents which may affect results and extrapolation of influences of various factors to PVC thermal degradation in solid state.

Polaron mechanism seems to be rich in features, consistent with most experimental observations, and it is hoped that recent interest in it may lead to further development of this mechanism.

4.2.8 DEGENERATED BRANCHING

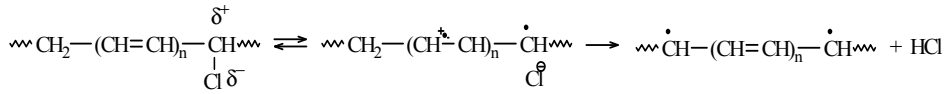
Troitskii and his group developed a mechanism of chain branching which is a combination of ionic and polaron mechanisms.[126,133,201,210-215] They came to the conclusion that polyenes in the excited triplet state (biradical state) may take part in the reaction of *cis-trans* rearrangement as well as in the other radical reactions, in particular, in the reaction of initiation of the thermal degradation of the polymer.[133]

In their mechanism the formation of the contact ionic pair is the first stage which is responsible for the rate of the reaction. It is then followed by fast splitting off of a proton with formation of HCl and olefin:



The double bond or the conjugated double bonds in the β-position to the chlorine atom has an accelerating effect on the thermal degradation of PVC.

In the excited triplet state, polyenyl carbocation is carbocation-biradical. The same active particle (ion-biradical pair) will form in the transition state of the thermal degradation of polyenyl fragments of PVC macromolecules. Then subsequent transformation of the ion-biradical pair into a biradical occurs by means of the splitting-off proton and its interaction with nucleophilic particle:[133]



This reaction yields a biradical which may react with a macromolecule, leading to initiation of the new chains of radical transformations of PVC. These two reactions represent the elementary acts of the degenerated chain branching.[133]

The mechanism agrees with experimental data obtained from degradation of PVC in solid state. Kinetical equations were also developed to verify features of this mechanism. It is an interesting concept which requires further work to broaden the scope of application of this mechanism. It should be noted that this mechanism follows some concepts of the polaron mechanism and it also shows that the mechanism of PVC degradation may need to be a combination of several different mechanisms.

4.2.9 TRANSITION STATE THEORY

Some of the previously discussed models are based on comparison of PVC degradation with dehydrochlorination of model compounds. Model compounds have simpler structure and high purity and therefore they may be more effectively studied. But they are not polymer and thus mechanisms stipulated by such studies must be verified. Frequently, comparison of activation enthalpy is commonly used for such verification. It should be noted that activation energy is not diagnostic of the mechanism. Even if the activation enthalpies are identical, it does not mean that the mechanisms are the same.[4]

Bacaloglu and Fisch[4] correlated activation enthalpies and entropies of different chloroalkanes, chloroalkenes and PVC to validate the model. Below, their reasoning is discussed to show benefits of using such validation theory, which is based on the transition state theory. The transition state theory assumes that molecules must traverse certain states (transition states) of potential energy higher than the average potential energies of either the reactant or product states in order to complete a reaction.[4] According to the Gibbs equation, the population of transition states is in statistical equilibrium with the reactant molecules:

$$\Delta G = \Delta H - T\Delta S \qquad [4.5]$$

where:

ΔG	free energy,
ΔH	enthalpy of activation,
ΔS	entropy of activation,
T	temperature.

The rate constant of any reaction is proportional to the concentration of molecules in the transition state and consequently determined by the free energy of activation. For each

mechanism of interaction between molecules or atoms of a molecule, the minimum activation free energy is reached only if certain geometrical conditions of the transition state are met.[4] Any changes in the structure of the reactants and/or the reaction conditions, such as state of aggregation or solvents, may affect the optimum geometry of the transition state, modifying both activation parameters.[4]

A reasonable correlation of activation enthalpy versus entropy for a series of reactions does not necessarily mean that they have the same mechanism, yet such a correlation is a far stronger support for it than a simple comparison of activation energies which may differ by 40-105 kJ/mol or more for the same mechanism.[4]

4.2.10 RECAPITULATION

The Merriam-Webster dictionary gives the following definitions of the word "mechanism":

> "a sequence of steps in a chemical reaction"
>
> "the fundamental physical or chemical processes involved in or responsible for an action, reaction, or other natural phenomenon"

Comparing these definitions with the above described mechanisms, we can make the following observations and suggestions for future studies:

- there is no a single mechanism which will include all the main steps observed in experimental studies,
- some research concentrates more on the type of reactions (e.g., ionic vs. radical) than on the required complex treatment of all experimental data within a framework of a comprehensive mechanism,
- there is evidence in experiment and its modelling that a comprehensive mechanism will not be homogenous (e.g., all ionic) but each step will depend on conditions and type of reactions,
- a comprehensive mechanism does not mean a set of chemical equations even with the most elaborate transition formulas if the physical component is not included,
- the physical component should relate chemical changes to the physical conditions of material, its physical changes, mechanical performance, and rates of their changes,
- a comprehensive mechanism should lay down a foundation for mathematical modelling of degradative processes with use of available kinetic data.

It is quite surprising that with new tools available, computer simulation is not used more frequently to verify older data produced on much slower computers (and thus limited in detail) than current, commonly available laptops. Concerted experimental and computational efforts will certainly improve currently known mechanisms and will simplify future developmental work.

4.3 KINETICS

4.3.1 INITIATION

In the previous section it was established based on literature data that dehydrochlorination is initiated mainly by chloroallylic and tertiary carbon labile structures. It is also suggested[4,6,216] that initiation begins from regular units from the beginning of the process[234] or after the labile groups have already been exhausted.[4,6] If initiation begins from labile structures it requires less energy and therefore it is a preferred pathway.[6]

A simple equation characterizes the act of initiation:

$$P \xrightarrow[k_i]{\Delta} P_1 + HCl$$

A PVC molecule, P, under the influence of heat has lost a molecule of HCl in an the act of initiation. The new polymer molecule, P_1, formed in this act contains one double bond if it was random elimination or elimination of tertiary chlorine or two conjugated double bonds if initiation began from allylic chlorine. Reaction rate of initiation, k_i, is the sum of many processes, as follows:

$$k_i = k_a + k_t + k_r + k_{ini} + k_{im} + k_o \qquad [4.6]$$

where:

k_i	initiation rate,
k_a	initiation rate by chloroallylic groups,
k_t	initiation rate by tertiary chlorine groups,
k_{ini}	initiation rate by rests of initiator,
k_{im}	initiation rate by impurities,
k_o	initiation rate by other non-accounted for influences (e.g., effect of atmosphere, or effect of temperature, or any catalytic substances); this constant may be a sum of these influences.

In order to simulate the initiation process and its rate, we would need to have all these constants or have methods of determining/calculating them. Having this, we would be able to predict and follow the influence of each process.

In addition to the above listed constants, Fisch and Bacaloglu[14] postulated introduction of two constants, k_1 which is constant of reaction which produces inactive polyenic structure (*trans* configuration) and k'_1 which is the reaction rate of active polyenic structure (*cis* configuration). This is also supported by Dean *et al*.,[12] although they have a different definition of inactive polyenes.

Regardless of the choice of constant, the initiation rate can be given by the following equation:

$$\frac{dP_1}{dt} = \sum_{i=0}^{j=n} k_{i_j}(P_{i_0} - P_{i_t}) \qquad [4.7]$$

where:

P_1	amount of double bonds formed,
t	time,

k_i constant of reaction catalyzed by any influential factor (see eq. 4.6),
j number of influential factors (1,2,3,...), e.g. a,t,r,... from eq. 4.6,
P_i initial concentration of defect i,
P_{i_0}
P_{i_t} concentration of defect i after time t.

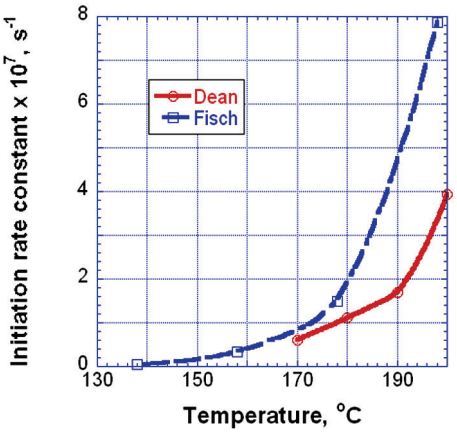


Figure 4.23. Initiation rate constants vs. degradation temperature. [Data from refs. 12 and 14].

Knowing the rate constants and concentrations of defects it will be possible to calculate the real rate of initiation. Until now, even the above equation was not proposed and constants of initiation rates for individual factors influencing initiation are not known. Future studies should address this issue, and unless it is resolved, thermal degradation kinetics is mostly a matter of speculation.

Today we have some data for constants of all initiation reactions bulked together. Bacaloglu and Fisch[6] show (Figure 4.14) that initiation rate constant increases with temperature. They also found that initiation rate constant was almost equal to the rate of constant of polyene sequence formation (e.g., rate constant at 198°C is 7.87 x 10^{-7} s^{-1} for initiation and 7.96 x 10^{-7} s^{-1} for double bond formation).[14]

Figure 4.23 shows that both studies arrived at a similar set of data. With temperature increasing initiation rate is accelerated and acceleration is non-linear.

Pyrolysis at temperatures above 250°C is a radical reaction. The initiation constant can be calculated from the following equation:[194]

$$k_1 = 3.43 \times 10^{13} \exp\left(\frac{-226000}{RT}\right) \qquad [4.8]$$

In some publications, we can find activation energy of initiation (Table 4.1).

Table 4.1. Activation energies of initiation of PVC dehydrochlorination.

Activation energy, kJ/mol	Reference
147	132
130	214
118	12
138	14
136	215
170	213[a]
234	59.1

a random elimination

Initial temperature of degradation is also of interest. Van Krevelen proposed the following relationship for calculation of the initial degradation temperature:[219]

$$T_{d,0} = 0.9\frac{\sum_i (Y_{d,1/2})_i}{M} \qquad [4.9]$$

where:

$T_{d,0}$	initial degradation temperature,
$Y_{d,1/2}$	molar half decomposition temperature,
M	molecular weight of repeating unit.

Arkadskii[220] proposed another equation:

$$T_{d,0} = \frac{\sum_i \Delta V_i}{\sum_i K_i \Delta V_i} \times 10^{-3} \qquad [4.10]$$

where:

ΔV_i	van der Waals volume of the repeating unit of the polymer,
K_i	the contribution of each atom of the structural unit to initial degradation of the polymer.

PVC initial degradation temperature calculated from these equations equals 205°C. It should be noted that this high calculated temperature is not caused by error of equations but equations do not consider labile structures, but only regular units. We may conclude that this should have been the initial degradation temperature of PVC if it did not have weak points developed during polymerization. We know from experimental studies that the higher the polymerization temperature, the lower the initial degradation temperature (because more defects are formed).[92]

4.3.2 PROPAGATION

Propagation produces HCl and polyene structures. For kinetic purposes, it is more exact to follow HCl in unstabilized PVC because polyene structures are affected by other reactions than propagation. There is no-ready-to-use kinetic equation available in literature. Since propagation is catalyzed by the presence of HCl, the kinetic equation of propagation can be written as follows:

$$\frac{dHCl}{dt} = k_{HCl}\left[\frac{dHCl}{dt} - \left(\frac{dHCl}{dt}\right)_d\right][PVC]_{ap} + \left[\frac{dHCl}{dt}\right]_0 \qquad [4.11]$$

where:

dHCl	amount of HCl splitting off in HCl catalyzed process in unitary time,
dt	unitary time,
k_{HCl}	constant of dehydrochlorination rate under catalytic influence of HCl,
$(dHCl/dt)_d$	rate of HCl diffusion (HCl which does not participate in catalytic process),
$[PVC]_{ap}$	active polyene (see explanations below),
$[dHCl/dt]_0$	rate of uncatalyzed process.

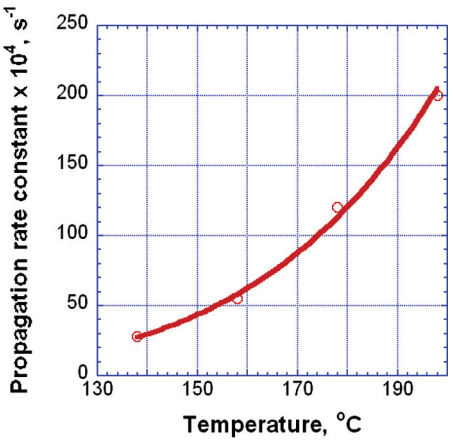


Figure 4.24. The effect of temperature on the dehydrochlorination rate of propagation. [Data from Fisch, M. H.; Bacaloglu, R., *J. Vinyl Additive Technol*., **1**, 4, 233-40, 1995.]

This equation is sufficiently simple to be useful in simulation processes. The rate of catalyzed dehydrochlorination is composed of two rates of random dehydrochlorination without the participation of HCl and the rate of catalyzed dehydrochlorination of growing polyenes. Considering the fact that some HCl produced in any of the two processes may escape by diffusion without any participation in the catalytic dehydrochlorination, this fraction of HCl stream is subtracted from potentially catalytic stream of HCl. For the process rate the concentration of active polyenes is also important. There are numerous reports included in this book which show that not all polyenes may undergo catalyzed dehydrochlorination (e.g., *trans* configuration, end of the chain and other defect structures do not support polyene growth), therefore they have to be excluded from participation.

In addition to simulation which permits estimation of constant and other parameters, the constant can also be determined by analysis. For example, Troitskii and Troitskaya[212] show that an uncatalyzed rate of dehydrochlorination can be approached by reprecipitation which destroys an original morphology of PVC (although it is possible to form new morphological structures capable to slow down diffusion of HCl). It should be noted that the reprecipitation also removes impurities which may catalyze dehydrochlorination.

Figure 4.24 shows that temperature affects the rate constant of propagation. If we compare these data with the rate of initiation (Figure 4.23), we find that the propagation rate is approximately 1000 times larger than the initiation rate. It should be noted that the propagation rate in Figure 4.24 is larger than k_{HCl} in equation [4.11] because it includes the rate of an uncatalyzed process.

Also, activation energy of propagation is low at approximately 52 kJ/mol (it is approximately 2.6 times lower than the energy of initiation). This may be due to the errors of estimation.[14] If this estimation is correct, this will suggest that the higher overall activation energy is caused by a combination of allylic chlorine (low activation energy is most likely the same as propagation), tertiary chlorine (higher activation energy) and random elimination (substantially higher activation energy). From thermogravimetrical analysis, activation energy appears to be almost constant at around 120 kJ/mol until about 60% HCl is removed.[222] At higher conversions it climbs up to 190 kJ/mol.[222] In another study, activation energy of propagation is estimated at 152.6 kJ/mol for unplasticized powder as determined by thermogravimetry and at 146.6 kJ/mol for plasticized film as determined by light absorption at 350 nm.[234] All these values are higher than most of the values in Table 4.1 for activation energy of initiation.

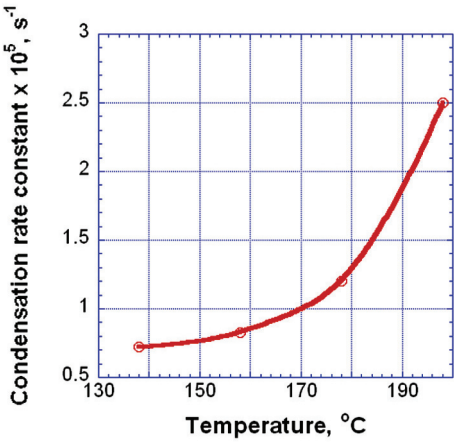


Figure 4.25. Effect of temperature on the rate of reaction of condensation to benzene. [Data from Fisch, M. H.; Bacaloglu, R., *J. Vinyl Additive Technol.*, **1**, 4, 233-40, 1995.]

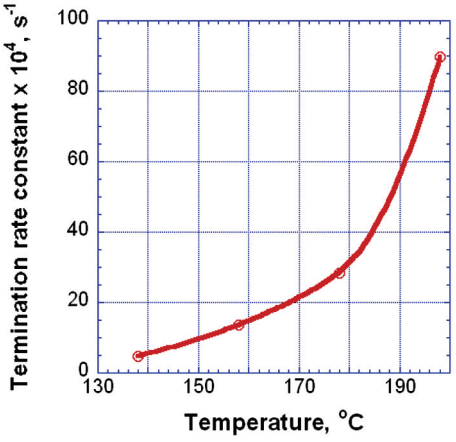


Figure 4.26. Chain termination rate constant vs. PVC degradation temperature. [Data from Fisch, M. H.; Bacaloglu, R., *J. Vinyl Additive Technol.*, **1**, 4, 233-40, 1995.]

The above discussion on propagation is restricted to HCl formation. Formation of aromatic compounds and oxidation of double bonds were not included yet. Oxidation processes were found to be relevant in the case of PVC thermal degradation below 200°C (see more on this subject in section 4.1.8). But there is no actual data on bleaching reaction (similar data exist on photobleaching, which reduces polyene length and color intensity; see more on this subject in the next chapter).

Benzene was found to be the only organic volatile product below 200°C.[5] Figure 4.25 shows that its rate of formation depends on temperature. It should be noted that the data in Figure 4.25 represent the difference between weight loss and emission of HCl, so they may not necessary include only benzene. The authors of the data[14] believe that the amount of benzene produced below 200°C is negligible. Formation of benzene has the lowest activation energy (~30 kJ/mol), because of the release of aromatic conjugation energy, but it also has the most severe conformational requirements for the transition state that decreases the activation entropy (~-230 kJ/mol). At higher temperatures (e.g., 250-500°C) such as exist in incineration processes, benzene is the major volatile product in the first stage of the process. There is no doubt that benzene is formed below 200°C since measurable quantities were determined by TG-GC-MS.[221]

4.3.3 TERMINATION

There are many reasons for polyene termination according to the available literature:

- configuration[3,5,14]
- crosslinking[23]
- Diels-Alder reaction[132,223]
- cyclization[132,223]
- recombination[194]

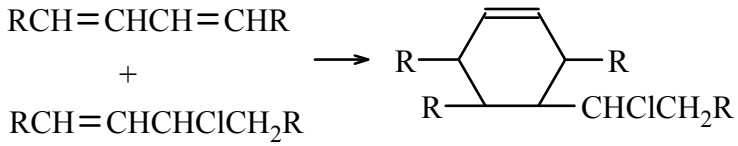
- HCl readdition[132]
- oxidation[187,224]
- electron density on terminal carbon atom (or inhibition of proton abstraction).[88,132]

Some authors believe that dehydrochlorination proceeds until the end without termination,[164,223] and many think that the termination mechanism has not been conclusively explained.[88,132,225]

Section 4.2.3 explains details of a six-center mechanism, which according to the authors[3,5,14] determines whether zip propagation continues or is terminated. We may add to it a graph which shows results of simulation of chain termination vs. temperature (Figure 4.26).[14] If this figure is compared with Figure 4.24, it becomes apparent that the process of termination is slower than the process of propagation but the rate of termination increases faster with temperature increasing. The activation energy of termination is higher than propagation (78 vs. 52 kJ/mol). Behnisch and Zimmermann[228] suggested that the increase in temperature favors gauche conformers and this is the reason for termination. This is contrary to the conclusions of Bacaloglu and Fisch.[3,5,14]

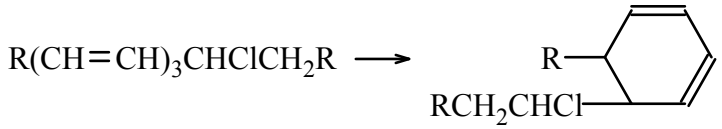
Crosslinking may be caused by the Diels-Alder reaction of recombination of radicals. In both cases, extension of polyene is interrupted.

The Diels-Alder reaction is given by the following equation:



Two potentially growing chains are interrupted by this reaction.

Diels-Alder cyclization is an intermolecular reaction given by the following equation:



One polyene is shortened and its growth interrupted by this reaction.

Radical recombination was proposed for higher temperature degradation such as exists in a pyrolytic reaction. Formed chlorine radical is very mobile but polyalkyl is not. This may cause recombination of two polyalkyl radicals and interruption of the reaction chain. HCl readdition is the process opposite to its splitting off. Some researchers believe that it has a probability to occur.[132] In the presence of oxygen many different reactions may occur which will interrupt growth of polyene.[187,224]

Molecular calculations were used in the pioneering work of Haddon and Starnes[198,226] to explain the cause of termination. MINDO/3 and *ab initio* STO-3G calculations were applied to analyze the electronic structures, equilibrium geometries, and

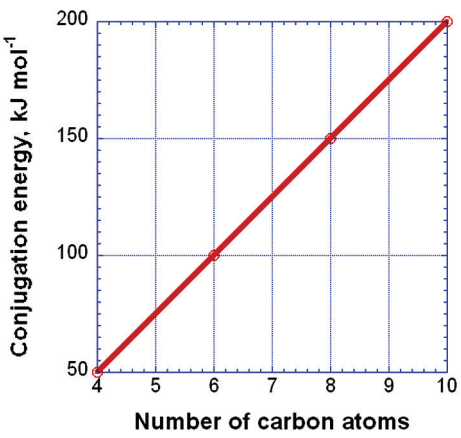


Figure 4.27. Energy of conjugation for linear polyenes vs. number of carbon atoms. [Data from Haddon, R. C.; Starnes Jr., W. H., *Adv. Chem. Ser.*, **169**, 333, 1978.]

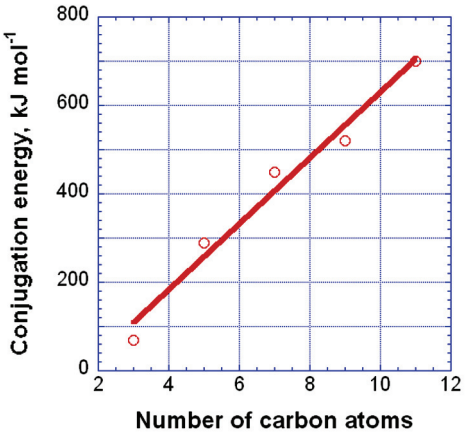
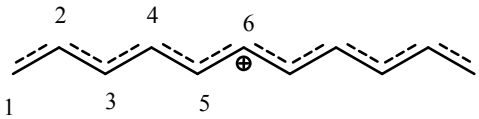


Figure 4.28. Energy of conjugation for linear polyenyl cations vs. number of carbon atoms. [Data from Haddon, R. C.; Starnes Jr., W. H., *Adv. Chem. Ser.*, **169**, 333, 1978.]

energy of the ground states of polyenyl cations and neutral polyenes. Technical aspects of calculations are omitted here since these can be found in the originals.

All bond angles and C–H bond length were assumed from available data, but bond length between any two carbon atoms, although initially imputed, was approximated by parabolic interpolation. Studies were done for linear polyenes having the following structure:

with two to ten carbon atoms, and for polyenyl cations:



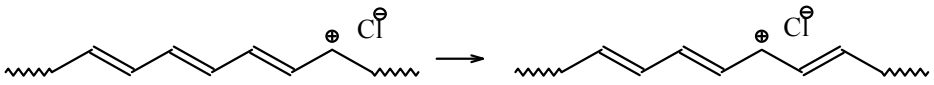
with three to eleven carbon atoms.

The conjugation energies of linear polyenes are given in Figure 4.27. The energy pattern shows that conjugation is favored, and that the energy depends on the number of conjugated double bonds. The conjugation energy of linear polyenyl cation is given in Figure 4.28. Since the reaction proceeds with a loss of conjugation and charge dispersal, the energy is higher and positive.

An alteration of charge density was observed; this means that even-numbered carbon atoms preferred to have a different sign of charge density than their odd neighbors.

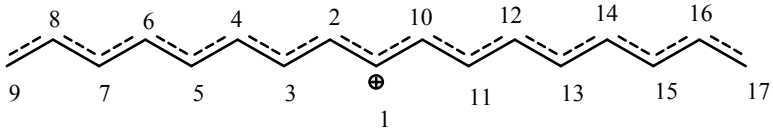
The authors[198,226] concluded that the forward reaction step is favored by unsaturation.

Since the charge is better established in the polyene center, there is a possibility of migration of an ion pair:



With increasing stabilization of the ion pair by unsaturation, the migration of the ion pair towards the center of the chain becomes more difficult, as does the abstraction of the proton, since the chloride ion is no longer in the neighborhood of the methylene group. Haddon and Starnes[198,226] noted that the charge density on methylene protons decreased along with increased unsaturation, which also does not favor elimination. This seems to explain why polyenes do not grow beyond a certain point.

Attracted by the success of these studies, we have decided to repeat the calculations using throughout the MINDO/3 method and better computer which allowed us to compare longer polyene cations and obtain comparable data for all polyene lengths.[88] Our calculations included polyenyl cations from C_3 to C_{17} for the following structure:



The structure is symmetrical, therefore the data for segment 9-1 are equivalent to those for segment 1-17. Under such circumstances only data for segment 1-9 are given below. Table 4.2 shows the length of carbon-carbon bonds, while Table 4.3 shows the total bond order.

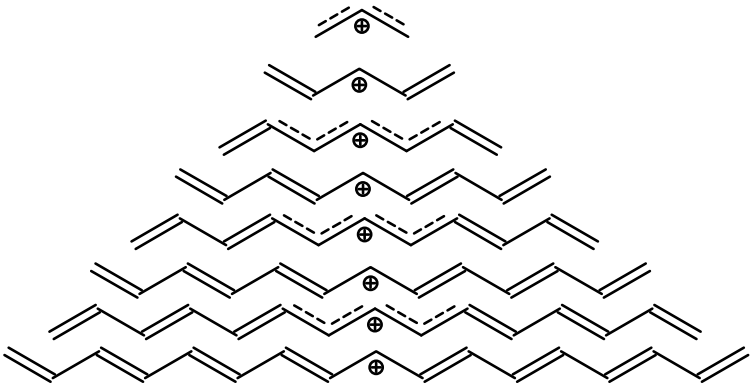
Table 4.2. The length of carbon-carbon bonds. [Data from Wypych, J., **Polyvinylchloride Stabilization**, Polymer Science Library, Jenkins, A. D., Ed., *Elsevier*, Amsterdam, 1986.]

Cation	Bond length, Å							
	9-8	**8-7**	**7-6**	**6-5**	**5-4**	**4-3**	**3-2**	**1-2**
C_3								1. 402
C_5							1.381	1.432
C_7						1.370	1. 440	1.411
C_9					1.376	1.445	1.396	1.420
C_{11}				1. 364	1.455	1.389	1. 434	1.411
C_{13}			1.360	1. 460	1. 382	1.442	1. 399	1.420
C_{15}		1. 359	1.463	1.377	1. 448	1.392	1. 430	1.411
C_{17}	1.359	1.463	1.375	1.451	1.386	1. 438	1. 401	1.419

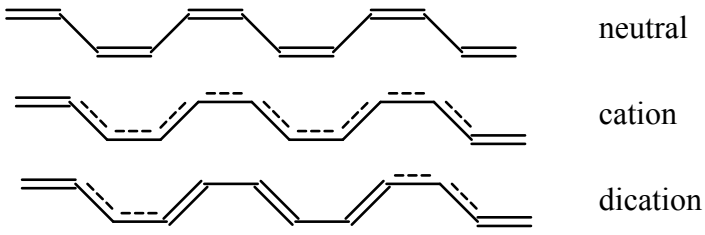
Table 4.3. The total bond order for polyene cations of varying length. [Data from Wypych, J., **Polyvinylchloride Stabilization**, Polymer Science Library, Jenkins, A. D., Ed., *Elsevier*, Amsterdam, 1986.]

Cation	Bond order (total)							
	9-8	**8-7**	**7-6**	**6-5**	**5-4**	**4-3**	**3-2**	**2-1**
C_3								1.703
C_5							1.813	1.541
C_7						1.864	1.460	1.666
C_9					1. 890	1.414	1.736	1.580
C_{11}				1.913	1.371	1.788	1.513	1.657
C_{13}			1. 927	1.343	1.824	1.461	1.717	1.590
C_{15}		1.937	1.323	1.805	1.420	1.763	1. 533	1.653
C_{17}	1. 943	1.311	1.868	1.390	1.799	1. 484	1.708	1.596

If we were to assign the formal double and single bonds to the results, the structures would appear as follows:



The longer the polyene, the more the double-bond character is observed, which may be related to the structure of polyenic cation assumed in our calculations, but Yamabe's work[227] shows that this is not the case. Yamabe has made similar calculations for C_{12} polyene and its single and double cations, as follows:



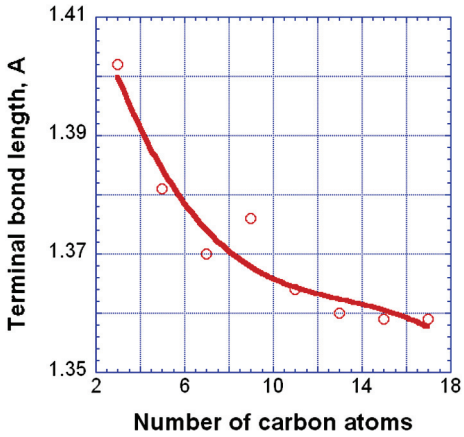


Figure 4.29. Terminal double bond length versus polyenic cation length. [Data from Wypych, J., **Polyvinylchloride Stabilization**, Polymer Science Library, Jenkins, A. D., Ed., *Elsevier*, Amsterdam, 1986.]

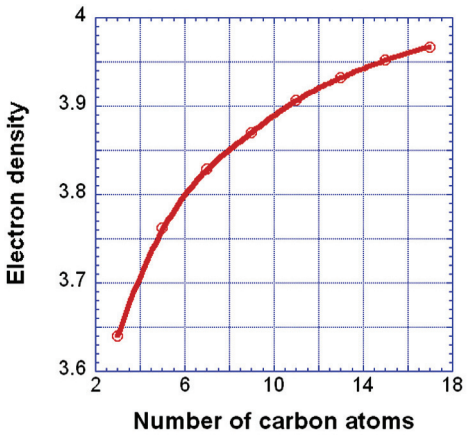


Figure 4.30. Electron density on terminal carbon versus polyenic cation length. [Data from Wypych, J., **Polyvinylchloride Stabilization**, Polymer Science Library, Jenkins, A. D., Ed., *Elsevier*, Amsterdam, 1986.]

The electron density follows the same pattern as the data given above. It is also evident that when polyene grows, the charge density differences between neighboring carbon atoms become smaller. The same pattern is favored when these differences between atoms in the center and close to the terminal carbons are compared.

The bond length and electron density for terminal carbons are given in Figures 4.29 and 4.30, respectively.

The bond order (total) is as follows:

Table 4.4. The bond order. [Data from Yamabe, T.; Matsui, T.; Akagi, K.; Ohzeki, K.; Shirakawa, H., *Mol. Cryst Liq. Cryst*., **83**, 125, 1982.]

Bond	1-2	2-3	3-4	4-5	5-6	6-7
neutral	1. 96	1. 28	1. 92	1. 30	1. 91	1. 30
cation	1. 85	1. 42	1. 69	1. 56	1. 62	1. 62
dication	1. 80	1. 56	1. 51	1. 80	1. 34	1. 88

The electron densities on particular carbon atoms from Stepien's and Wypych's work are given in Table 4.5.

Table 4.5. The electron density on each carbon atom. [Data from Wypych, J., **Polyvinylchloride Stabilization**, Polymer Science Library, Jenkins, A. D., Ed., *Elsevier*, Amsterdam, 1986.]

Cation	Carbon atom number								
	9	8	7	6	5	4	3	2	1
C_3								3.640	4.259
C_5							3.762	4.225	3.696
C_7						3.829	4.208	3.753	4.213
C_9					3.870	4.194	3.799	4.207	3.773
C_{11}				3.907	4.179	3.836	4.198	3.792	4.211
C_{13}			3.932	4.167	3.868	4.187	3.817	4.208	3.797
C_{15}		3.952	4.157	3.895	4.175	3.843	4.201	3.809	4.211
C_{17}	3.967	4.148	3.917	4.163	3.867	4.193	3.826	4.209	3.809

The above seems to explain why polyenes have to terminate. As double bond length is already stabilized, and, more importantly, electron density is approaching value of 4, there is gradually less of an effect on the neighboring monomer unit, which becomes a regular unit in the PVC chain, and thereby the HCl can be eliminated (as from any other regular unit) only by random elimination.

In addition, we have calculated the ionization potential given in Figure 4.31.

Since the ionization potential value decreases with polyene increasing, it may explain why temperature increase and the presence of oxygen are so detrimental for longer polyenes.

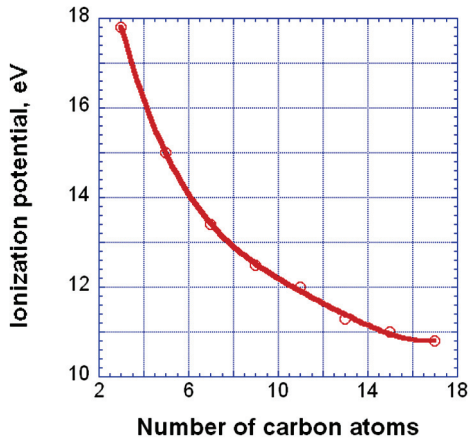


Figure 4.31. Ionization potential versus polyenic cation length. [Data from Wypych, J., **Polyvinylchloride Stabilization**, Polymer Science Library, Jenkins, A. D., Ed., *Elsevier*, Amsterdam, 1986.]

Stepien's and Wypych's explanations,[88] although slightly different from those presented by Haddon and Starnes,[198] lead to a similar conclusion: there is a natural mechanism which does not promote polyenes growth above a certain limiting length.

Meier and Kip have rejected the above results of MINDO/3 calculation on the ground that MINDO/3 method is inadequate (arguments of such conclusion are included in their paper).[199] AM1 method was selected by Meier and Kip which, according to them, was the preferred method of studying such systems. Using their method and settings they arrived at the conclusion that "HCl abstraction from PVC is about as probable as HCl abstrac-

tion adjacent to a polyene sequence, therewith indicating that polyene lengthening is not promoted by any such difference." This statement contradicts accepted studies which lead us to believe that labile segments initiate the process of degradation which propagates by a zip mechanism until it ends by a not fully agreed upon termination mechanism.

Very few papers give information on polyene length. Meier and Kip[199] believe that this length is at least 65 conjugated bonds (based on their Raman studies) or 22 (if ionic mechanism is accepted). Gerrard and Maddams[229] estimated the polyene length as between 17 and 20 conjugated double bonds. In another paper, Gerrard *et al.*[230] found the presence of 30 double-bond long polyene sequences by Raman spectroscopy. Similar data have been obtained for degradation in the presence of oxygen (16-20).[224]

The length of polyenes depends on temperature of degradation (it decreases with temperature increasing),[228,231] presence of oxygen,[187] presence of HCl (autocatalysis increases polyene length),[191] and it increases with syndiotacticity increasing.[232]

It is very difficult to define the range of polyene length based on this data, especially since some issues were found with application of Raman spectroscopy in these studies, and Raman spectroscopy is the major source of information about these very long polyenes.[233]

It is not less difficult to postulate the mechanism of termination. All chemical reactions and proposed mechanisms discussed in this section seem to have credible supportive information. Only two mechanisms seem to be generic: mechanism proposed by the Bacaloglu and Fisch[14] and that proposed by Wypych and Stepien.[88] In both cases, there are critical views of some scientists who studied this subject. It is therefore hoped that further efforts will either reject these mechanisms or clarify uncertainties.

4.4 RESULTS OF THERMAL DEGRADATION

4.4.1 VOLATILES

Composition of volatiles depends on temperature. Figure 4.32 shows information on composition of volatiles at different temperatures. HCl is the only volatile product emitted at 160°C and 180°C.[234] At 200°C a substantial amount of organic compounds is produced. These organic compounds are found to be benzene. Similar is the composition at 220°C, whereas it changes at 240°C and 280°C. At these two temperatures many other organic compounds are produced which are discussed below. The HCl fraction in volatiles decreases with time, most likely because the labile group effect is stronger in the beginning of dehydrochlorination, later displaced by propagation and random initiation. At 280°C, fraction of emitted HCl increases with time increasing, which is probably caused by the influence of HCl catalyzed dehydrochlorination.

In addition to HCl, the following groups of volatile organic materials are emitted depending on conditions of degradation:[33]

- aromatic hydrocarbons (they are the main source of smoke)
- aliphatic hydrocarbons
- chlorinated aliphatics
- chlorinated aromatics (monochlorobenzene, chlorotoluene, and benzyl chloride).

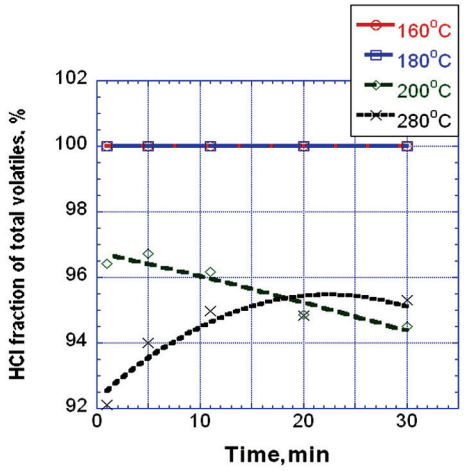


Figure 4.32. HCl fraction in volatiles vs. time at different temperatures. [Data from Statheropoulos, M., *J. Anal. Appl. Pyrolysis*, **10**, 89-98, 1986.]

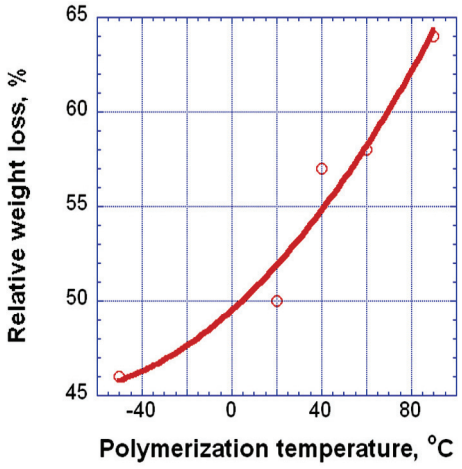


Figure 4.33. Relative weight loss due to dehydrochlorination vs. polymerization temperature. [Data from Gonzalez, N.; Mugica, A; Fernandez-Berridi, M. J., *Polym. Deg. Stab.*, **91**, 4, 629-633, 2006.]

There are some toxic substances emitted at low concentrations. These will be discussed below in a a separate chapter.

No oxygen containing volatiles have been found. Products of oxidation are formed in polymer and transformed to tar. There is no substantial difference between the composition of volatiles produced under nitrogen and during degradation in air atmosphere.[33]

The amount of chlorinated aromatics increases with temperature of degradation and their concentration is much higher than the concentration of chlorinated aliphatics. Two stage vacuum pyrolysis performed at 360°C and 520°C permits recovery of 99.11% HCl.[235] Benzene is produced at lower temperatures (below 240°C).[234] At higher temperatures toluene becomes a major volatile organic product.[221]

4.4.2 WEIGHT LOSS

Figure 4.33 shows the effect of polymerization temperature of PVC on its weight loss.[236] The weight loss increases with polymerization temperature increasing, which is consistent with mechanisms of degradation because increased temperature of polymerization contributes to a higher concentration of labile groups.

Figure 4.34 shows that the weight loss obtained from measurement of HCl matches exactly weight loss measured by thermogravimetry. Only at higher temperatures there is some difference because the thermogravimetric method accounts for organic volatiles. Thermogravimetric (or any weight) measurements are even more complicated when PVC contains plasticizers. Aging studies at lower temperatures (85-110°C) show that at this range of temperatures only plasticizer is lost.[237] If temperature increases further, the gravimetric methods will give a sum of plasticizer and HCl lost in the process.

A thermogravimetric study of degradation in oxygen and nitrogen at 210°C show that the weight loss under oxygen is 2.1 to 3.7 times higher than under nitrogen.[186] This is

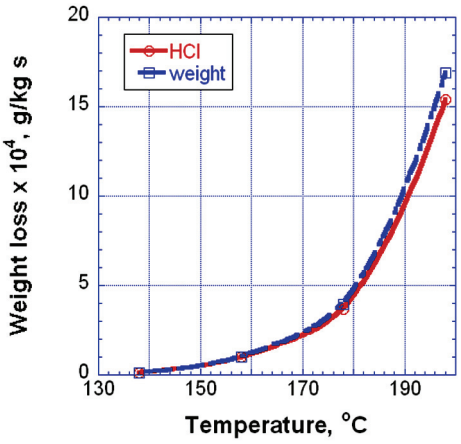


Figure 4.34. Weight loss vs. degradation temperature. [Data from Fisch, M. H.; Bacaloglu, R., *J. Vinyl Additive Technol*., **1**, 4, 233-40, 1995.]

in contradiction to the studies reported in the previous section,[33] which showed that there was no difference in volatile products obtained under air and nitrogen and that volatile products did not contain oxygen.

4.4.3 CHAR FORMATION

PVC pyrolysis and PVC fires result in formation of char. Both processes have different requirements. In PVC pyrolysis, the goal is to reduce/eliminate char formation because char causes a loss of calorific value of PVC as a fuel and char forms a solid material which has to be disposed of and it must be removed from equipment, which interrupts the process and makes it more expensive.[33,221,235,238-239] In fire protection, maximizing the char formation is an essential goal of formulating because conversion to char reduces the amount of flammable volatiles and smoke formation.[240-242]

Vacuum pyrolysis of PVC at temperatures up to 500°C results in formation of 9.5% char.[33] The char is formed in the temperature range of 360-520°C.[235] The char formation depends on temperature. More char is formed at elevated temperatures. With temperature increasing, char becomes more aromatic.[235]

Formation of char can be reduced (or almost eliminated) by addition of oxygen and/or steam.[238] Char reacts with steam to form H_2 and CO (syngas).[239]

Because of high concentration of chlorine, PVC is inflammable but additives reduce its natural abilities (especially some plasticizers). In some cases, PVC is formulated with flame retardants of various nature which, among other features, are able to reduce volatiles. Volatiles are flammable, therefore flame retardant formulations aim at reducing their concentration. Volatile components contribute to smoke and it is important to decrease smoke formation by use of flame retardants.[240-242]

4.4.4 ASH CONTENT

Ash formation depends on inorganic load. Pure PVC has only traces of inorganic compounds, therefore its incineration does not leave ash residue. This is not true with compounded PVC, which may contain metal salts from stabilizers and fillers.

4.4.5 THERMAL LIFETIME

Dakin's kinetic equation

$$-\frac{dP}{dt} = Af(P)\exp\left(-\frac{E}{RT}\right) \qquad [4.12]$$

where:

P	mechanical or electrical property of interest,
f(P)	differential function of degradation,
A	constant,
E	activation energy,
R	gas constant,
T	temperature.

is often used for determination of lifetime of materials. After integration and transformation, the following equation is obtained:[243]

$$\ln t_u = \ln t_a + \frac{E}{T}\left(\frac{1}{T_u} - \frac{1}{T_a}\right) \qquad [4.13]$$

where:

t_u	lifetime
u,a	aging at temperature of use and temperature of accelerated aging, respectively.

No such data is available in literature.

4.4.6 OPTICAL PROPERTIES

4.4.6.1 Color change

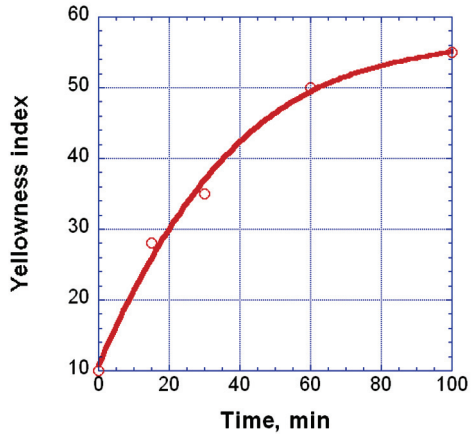


Figure 4.35. Yellowness index of PVC vs. exposure time to 180°C. [Data from Arkis, E.; Balkoese, D., *Adv. Polym. Technol.*, **21**, 1, 65-73, 2002.]

Figure 4.35 shows the effect of thermal degradation on color change measured by yellowness index.[244] Color changes more rapidly in the beginning, then it levels off. This is because the color changes initially to red and eventually to black. Only initial color can be determined correctly by colorimetric measurements because more saturated colors cannot be measured with precision.

Wavelet transform of photoacoustic spectra was used to determine polyene growth in PVC.[245] The method permits measurement of concentration of polyenes of different lengths. The distribution of polyenes could be measured successfully in the presence of stabilizers to help in understanding their mechanism of action and in virgin PVC to demonstrate that polyene length increases during degradation.[245]

In another experiment,[246] sample strips were aged in an oven at different temperatures and time intervals. Degraded specimens were then measured with scanner to determine RGB color values which were then compared with a number of double bonds formed in the degradation process.

These examples are given to show that many problems of degradation and stabilization would have been solved if there was a proper analytical methodology capable of measuring length distribution of growing polyenes, HCl emission, and color change in the same experiment. The above contributions attempt to generate some of these data but the methods are still too crude to provide comprehensive data required for degradation and stabilization modelling.

4.4.6.2 Extinction coefficient

Bacaloglu *et al*.[247] found that the extinction coefficient for a double bond increases from 23,200 for a polyene with 6 conjugated double bonds to 29,954 for a polyene with 28 conjugated double bonds. Based on RGB extinction (see the previous section) they can calculate the apparent coefficient of extinction from the following equation:

$$\varepsilon = \frac{E_{rgb}}{Lc_{DB}} \qquad [4.14]$$

where:

E_{rgb}	RGB extinction,
L	length of the light penetration (thickness of sample),
c_{DB}	double bond concentration.

The above equation can also be used to determine double bond concentration (see the next section). The RGB extinction depends linearly on the total concentration of double bonds, proving the validity of the Lambert-Beer law for reflectance of PVC.[246]

The concentration of polyene sequences was also calculated from the UV data using an equation similar to [4.14] but for absorbance at a particular wavelength.[130] In this case, the extinction coefficient was calculated using a method developed by Popov and Smirnov:[248]

$$\varepsilon_\lambda = 10,000 + [20,000(n-1)] \qquad [4.15]$$

where:

n	polyene sequence length.

4.4.6.3 Absorbance

Bacaloglu and Fisch[6,7,248] used the scanning method discussed in the previous section and equation [4.14] to determine polyenes of different lengths. Figure 4.36 shows that polyenes can be measured in different ranges of the spectrum and their length correlates with the wavelength of absorbed radiation. This data permits determination of molar absorptivities which can be then used to calculate the number of conjugated double bonds from equation:

$$\varepsilon = 31,800n - 51,700 \qquad [4.16]$$

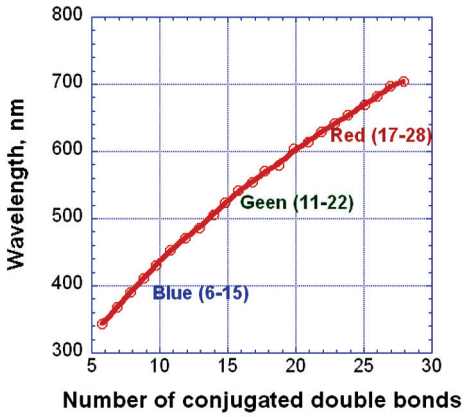


Figure 4.36. Wavelength of absorbed light in visible region vs. number of conjugated double bonds in polyene. [Data from Bacaloglu, R.; Stewen, U., *J. Vinyl Additive Technol.*, **7**, 3, 149-155, 2001.]

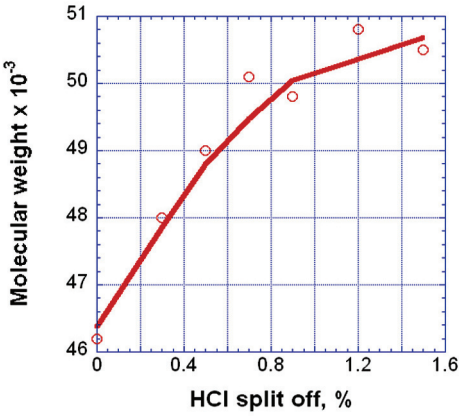


Figure 4.37. Molecular weight vs. amount of HCl eliminated in process of dehydrochlorination under inert gas. [Data from Hjertberg, T.; Martinsson, E.; Sorvic, E., *Macromolecules*, **21**, 603-609, 1988.]

The above method leads us in the right direction even though it is still too complicated to use on a larger scale of experiments and prone to errors due to the fact that separate samples have to be used for each point of measurement.

Wypych *et al*.[249] developed a continuous method of measurement of light reflected from a sample during its degradation. The method is discussed in Chapter 10 and the results of measurements in Chapter 11.

Owen *et al*.[84] found that absorbance at 610 nm changes with degradation time and they used these measurements to monitor polyene formation. Absorbance also changes in the UV region for short polyenes and shows a series of peaks relative to different polyene length.[250,251] Short sequences (3-4 double bonds) were monitored at 267 nm and longer sequences (6-8 double bonds) at 347 nm.[252]

For propagation reactions, the syndiotactic content is essential and it can be measured by a ratio of IR absorbance at 1428 and 1434 cm^{-1}.[253]

4.4.7 MOLECULAR WEIGHT

It is well established that chain scission has minor influence on molecular weight changes if degradation occurs in oxygen-free atmosphere (e.g., under vacuum or inert gas). During photooxidation, the oxidation occurs in the vicinity of the double bond, resulting in chain scission.[254] On the other hand, the crosslinking reactions occur under aerobic and anaerobic conditions.

Figure 4.37 shows the relationship between dehydrochlorination and molecular weight.[127] Molecular weight gradually increases during the dehydrochlorination process. Benavides *et al*.[255] show that at lower temperatures of degradation (160 and 170°C) molecular weight of polymer stays constant and increases above these temperatures. It is fairly well established that crosslinking reactions are dominant during PVC incineration as well as in formulations containing flame retardants.

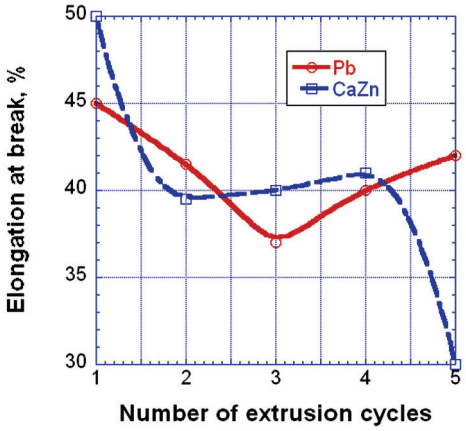


Figure 4.38. Elongation vs. number of extrusion cycles. [Data from Ditta, A. S.; Wilkinson, A. J.; McNally, G. M.; Murphy, W. R., *J. Vinyl Additive Technol.*, **10**, 4, 174-178, 2004.]

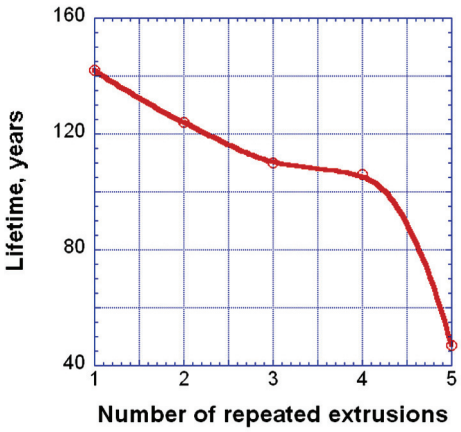


Figure 4.39. Lifetime of PVC material vs. number of extrusion cycles. [Data from Yarahmadi, N.; Jakubowicz, I.; Gevert, T., *Polym. Deg. Stab.*, **73**, 1, 93-99, 2001.]

4.4.8 MECHANICAL PROPERTIES

It is seldom found that thermal degradation affects mechanical properties. It is not because thermal degradation does not affect mechanical properties but because stabilization prevents excessive damage which may cause noticeable changes in mechanical properties. This can be seen from Figure 4.38. If PVC is stabilized with lead stabilizer which offers very long protection, then elongation only initially decreases because morphological changes affect mechanical properties. This is followed by elongation increase. PVC stabilized with calcium/zinc stabilizer reacts initially in the same manner but then elongation drops down substantially because catalytic influence of $ZnCl_2$ rapidly increases deterioration rate.

Figure 4.39 shows that after repeated extrusions, product lifetime decreases. In the beginning, this decrease is slow and then it becomes more dramatic. Stabilization prevents more extensive deterioration as long as active stabilizer has a suitable concentration.

The above examples are a good demonstration of damage done to mechanical performance by conditions of processing. Figure 4.40 illustrates possible damage by exposure to much lower temperatures – such as may be met by PVC products during their use. Creep resistance of PVC material deteriorates during exposure to as low a temperature as 90°C.

4.4.9 ELECTRIC PROPERTIES

Figure 4.17 shows volume resistivity changes vs. temperature of aging for 1000 h. Rapid increase of deterioration of volume resistivity occurs at 140°C with much smaller changes at lower temperatures. Figure 4.41 shows changes of dielectric loss factor at two temperatures. At 120°C there is no change during 1000 h exposure but at 140°C there is rapid increase in the dielectric loss factor. Similar data are available for dielectric constant and breakdown strength.[168]

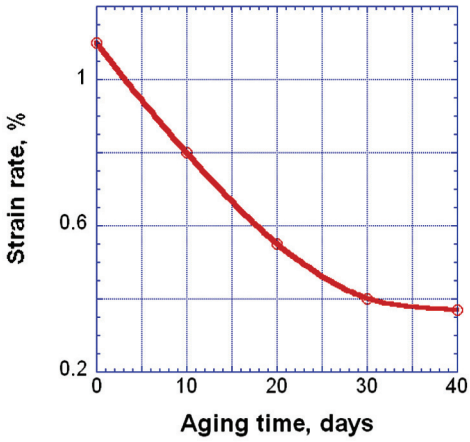


Figure 4.40. Strain rate vs. aging time. [Data from Hamza, S. S.; Abdel-Hamid, M., *Polym. Deg. Stab.*, **62**, 1, 171-174, 1998.]

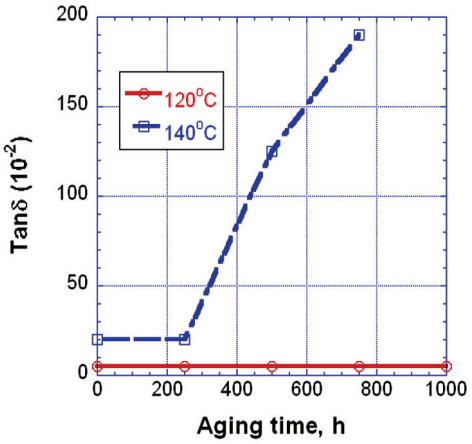


Figure 4.41. Dielectric loss factor vs. aging time at different temperatures. [Data from Nedjar, M.; Beroual, A.; Boubakeur, A., *J. Appl. Polym. Sci*., **102**, 5, 4728-4733, 2006.]

PVC degradation occurs in two steps. First, the plasticizer evaporates. The plasticizer molecules diffuse towards the surface. Plasticizer present on the surface quickly evaporates. This initiates the bulk diffusion which is the reason for rapid deterioration around 140°C. At the second stage of degradation, material changes color and begins to emit HCl.[168]

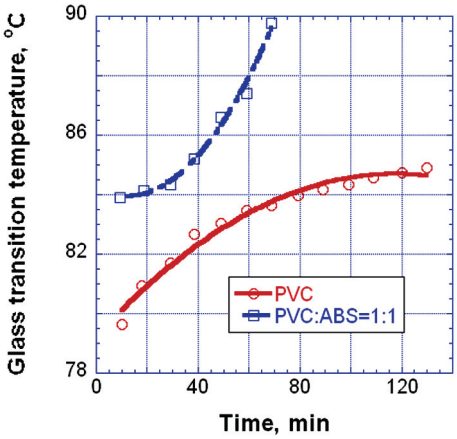


Figure 4.42. Changes of glass transition temperature of pure PVC and its 1:1 blend with ABS during exposure to 200°C. [Data from Braun, D.; Koemmerling, S., *Angew. Makromol. Chem.*, **195**, 3448, 205-211, 1992.]

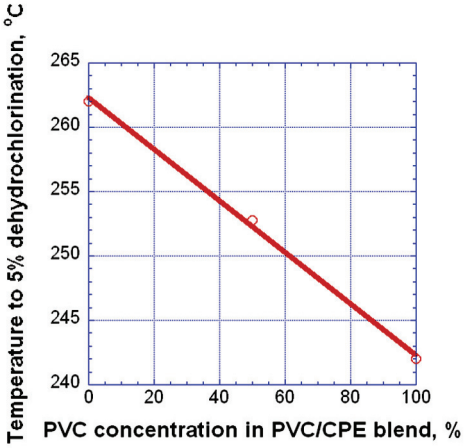


Figure. 4.43. Effect of concentration of PVC in PVC/CPE blend on temperature to 5% mass loss in thermogravimetric determination. [Data from Vrandecic, N. S.; Klaric, I.; Kovacic, T., *J. Thermal Anal. Calorimetry*, **74**, 1, 171-180, 2003.]

4.5 EFFECT OF ADDITIVES

4.5.1 BLEND POLYMERS

4.5.1.1 ABS

ABS/PVC blends are incompatible. In the full range of concentrations, blends have two glass transition temperatures very close to the glass transition temperatures of the component polymers.[259] Figure 4.42 shows the effect of addition of ABS on PVC thermal degradation.[260]

These blends offer some technical advantages, such as increased heat deflection temperature[261] of PVC or improved flame retardant properties of ABS,[262] but at the same time thermal stability suffers as Figure 4.42 shows. The thermal stability is decreased because of the influence of butadiene segments in ABS which accelerate PVC thermal and oxidative degradations.[260,263]

4.5.1.2 ASA

Poly(vinyl chloride)/acrylonitrile–styrene–acrylate, ASA copolymer blend with good ultraviolet irradiation resistance and toughness was reported.[265] ASA is known to have excellent UV resistance toughness.[265] Addition of ASA to PVC improved its heat resistance, thermal stabilization, and protected PVC from photochemical degradation.[265]

4.5.1.3 Chlorinated polyethylene, CPE

Chlorinated polyethylene is a common impact modifier,[264] and compatibilizer of PE/PVC blends.[266] It also increases filler intake.[264] Figure 4.43 shows that CPE has better thermal stability than PVC and that thermal stability of blend is proportional to their concentration in the blend.[267] It is also noticeable that addition of CPE increases fusion temperature but flow properties of blend are improved, which shortens the time of processing and

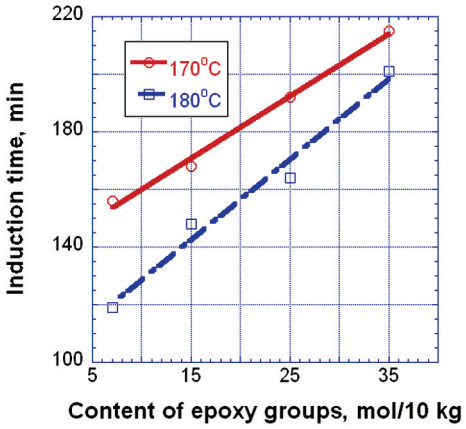


Figure 4.44. Induction time vs. content of epoxy groups on butadiene/styrene triblock copolymer compounded with PVC (blend contains 10% copolymer). [Data from Meissner, W.; Zuchowska, D., *Polym. Deg. Stab.*, **60**, 415-424, 1998.]

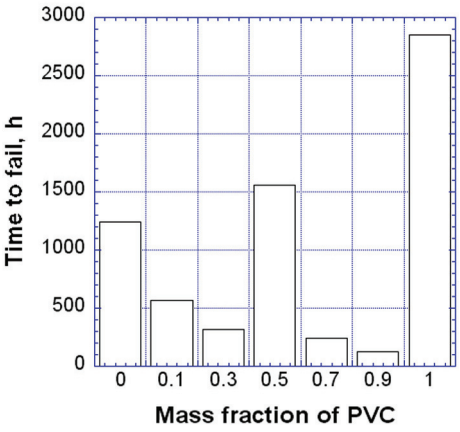


Figure 4.45. Time to fail vs. mass fraction of PVC in blends with EVA (70% VA). Degradation temperature 200°C. [Data from Monteiro, E. E. C.; Thaumaturgo, C., *Composites Sci. Technol.*, **57**, 8, 1159-1165, 1997.]

improves effect.[268] Stabilizing composition for polymer blends including PVC/CPE blends contains phenolic antioxidant, process stabilizer, and glycidyl(meth)acrylate copolymers.[269]

4.5.1.4 Epoxidized butadiene/styrene block copolymer

Epoxidized butadiene/styrene block copolymer compounded with PVC behaves like epoxy stabilizer by reacting HCl. Figure 4.44 shows that its rapid reaction decreases dehydrochlorination in proportion to the amount of epoxy groups present in the system.[263] The authors of the contribution[263] also suggest that the presence of the copolymers facilitates readdition of HCl into PVC backbone.

4.5.1.5 Epoxidized natural rubber

Epoxidized natural rubber forms miscible blends with PVC at any concentration. It is a good impact modifier but it has very poor thermoxidative stability which limits its application.[270,271]

4.5.1.6 Ethylene vinyl acetate, EVA

Ethylene vinyl acetate is a known impact modifier of PVC.[272] Its copolymer with carbon dioxide, EVA-CO improves heat distortion temperature of PVC.[273] EVA has a plasticizing effect on PVC.[47,274] Its equimolar blend with PVC gives plasticizer-free low-fogging film which can be used in tarpaulins, roofing sheets, and pond liners.[47] There is some disagreement regarding EVA miscibility with PVC. It is regarded as miscible,[275] miscible in a narrow range of vinyl acetate content (65-70%),[274] and its miscibility increases with CO content increasing in EVA-CO.[278]

There is an agreement regarding thermal stabilities of polymers and blends but details depend on chemical composition. EVA generally has better thermal stability than

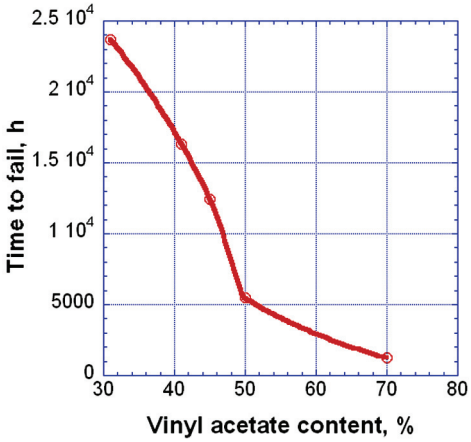


Figure 4.46. Time to fail of EVA having different contents of vinyl acetate. Degradation temperature 200°C. [Data from Monteiro, E. E. C.; Thaumaturgo, C., *Composites Sci. Technol*., **57**, 8, 1159-1165, 1997.]

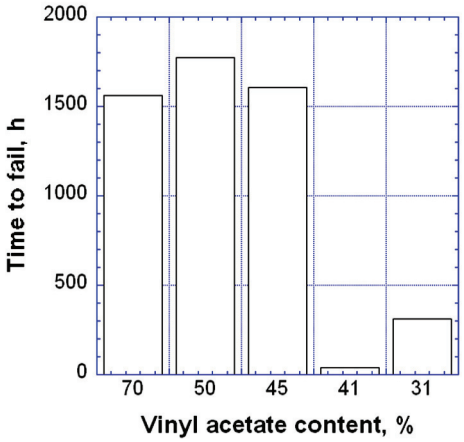


Figure 4.47. Time to fail of PVC/EVA=1:1 blends with EVA having different contents of vinyl acetate. Degradation temperature 200°C. [Data from Monteiro, E. E. C.; Thaumaturgo, C., *Composites Sci. Technol*., **57**, 8, 1159-1165, 1997.]

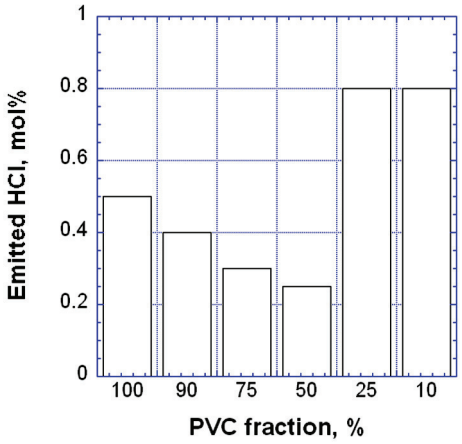


Figure 4.48. The amount of emitted HCl during 5 h at 180°C under nitrogen for PVC/HIPS blends having different PVC concentrations. [Data from Braun, D.; Boehringer, B.; Eidam, N.; Fischer, M.; Koemmerling, S., *Angew. Makromol. Chem*., **216**, 3865, 1-19, 1994.]

PVC.[244,277] Blending PVC with EVA produces materials which have lower thermal stability than component polymers (Figure 4.45).[217,277] At the same time, the EVA grades which are more thermally stable (Figure 4.46) decrease more extensively the thermal stability of blends with PVC (Figure 4.47). Figure 4.45 shows that all blends have lower thermal stability than PVC. Figure 4.46 shows that EVA having less than 70% vinyl acetate is substantially more stable than PVC. At the same time blends of these thermally stable EVA copolymers with PVC have very low thermal stability (Figure 4.47). This probably is caused by very narrow miscibility[274] of PVC and EVA. Only in the range of their miscibility their blends perform well. The data shows that the best strategy in development of these blends is to use 1:1 blends of PVC with EVA having 65-70% vinyl acetate.

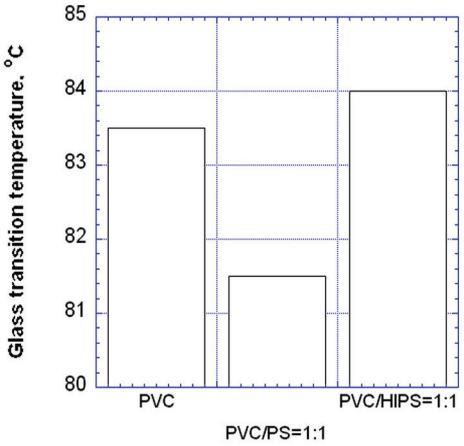


Figure 4.49 Glass transition temperature of PVC and its blends after annealing at 200°C for 100 min. [Data from Braun, D.; Koemmerling, S., *Angew. Makromol. Chem.*, **195**, 3448, 205-211, 1992.]

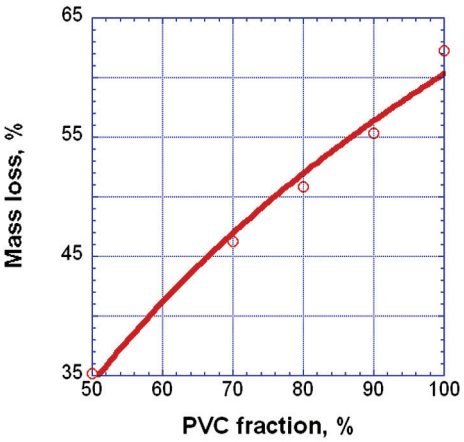


Figure 4.50. Mass loss vs. PVC fraction during thermogravimetric study of PVC/MBS blends. [Data from Andricic, B.; Kovacic, T., *Polym. Deg. Stab.*, **65**, 1, 59-64, 1999.]

4.5.1.7 High impact polystyrene, HIPS

Figure 4.48 shows that the thermal stability of the blends increases with increasing HIPS content up to 50 wt%. At higher HIPS content, thermal stability of blend decreases.[278] This reverse behavior is based on two different influences of HIPS. PS stabilizes PVC, whereas the C=C double bonds of polybutadiene are responsible for a destabilization of PVC. This antistabilizing effect becomes significant at high concentrations of HIPS. Figure 4.49 confirms this behavior. Full data on glass transition temperature show that glass transition of PVC/PS changes very little with time of annealing, whereas for PVC and its blend with HIPS, changes of glass transition temperature are substantially larger.

4.5.1.8 Methylmethacrylate-butadiene-styrene

Polymeric modifiers of PVC improve the heat deflection temperature, act as plasticizers, processing aids, and impact modifiers. Modifying agents may considerably influence the thermal stability of the blend. The degradation products of the blend may influence the rate of degradation, but in some cases they may act catalytically or inhibit the degradation processes. Their influence depends on the miscibility of blend components, the presence of double bonds, etc. Methylmethacrylate-butadiene-styrene terpolymer (MBS), is one of the most effective impact strength modifiers of PVC and it is added in large concentrations (up to 20%).[279] Figure 4.50 shows that MBS decreases the dehydrochlorination rate, mostly by dilution. MBS and its blends are prone to oxidative degradation of its rubber phase under oxygen and heat.[280] Combination of a sterically hindered phenolic antioxidant(s) and thioether was used for stabilization of MBS and its blends with PVC with a success.[280] In another development, isoindolo[2,1-a]quinazoline derivatives were proposed for stabilization of organic materials against light, oxygen, and heat.[281] MBS and its

blends with PVC can also be stabilized by this stabilizer.[281] PVC and its blends with MBS benefit from stabilization with polymeric and copolymeric phosphites discussed in invention.[282]

4.5.1.9 Methylmethacrylate-isoprene-styrene, MIS

Methylmethacrylate-isoprene-styrene having core-shell structure, obtained by seed emulsion polymerization, were used as a toughening agent for PVC.[283] MIS toughening gave a better results than MBS toughening, especially when the isoprene content was about 70%.[283]

4.5.1.10 Nitrile rubber, NBR

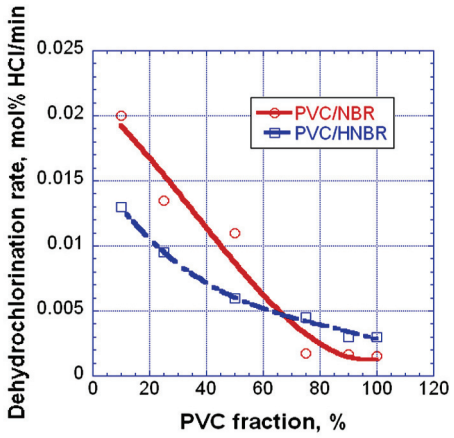


Figure 4.51. Dehydrochlorination rates of PVC/NBR and PVC/HNBR blends vs. PVC fraction. [Data from Braun, D.; Boehringer, B.; Eidam, N.; Fischer, M.; Koemmerling, S., *Angew. Makromol. Chem*., **216**, 3865, 1-19, 1994.]

PVC/NBR blends are perhaps the oldest commercial blends. They were introduced about 60 years ago. NBR acts in the blend as a permanent plasticizer[284,285] in numerous commercial applications, including wire and cable insulation in which PVC improves the chemical resistance, thermal ageing and abrasion resistance of NBR. PVC forms a miscible blend with NBR as evidenced from a single glass transition temperature, which is intermediate between that of the pure components.[284] Figure 4.51 shows that NBR increases dehydrochlorination rate. It is usually explained by interaction between unsaturated bonds and HCl. In the range of 200 min of degradation at 180°C presented in Figure 4.51 such influence is rather small. If degradation is continued there is a substantial difference between NBR and hydrogenated NBR. This shows that the effect of double bonds is only felt at more advanced stages. Figure 4.51 shows that both NBR and HNBR increase dehydrochlorination rate in proportion to their concentration. This increase is explained by an interaction between the PVC chains and the nitrile group. This influence is expected to be similar to that experienced with other polymers containing acrylonitrile groups, including polyacrylonitrile (see section 4.5.1.11).[278] UV degradation is prevented by coating products with PVC/NBR blend with poly(vinyl alcohol) containing nanoparticles of titanium dioxide.[286] Thermal conductivity, thermal diffusivity, and specific heat capacity of PVC/NBR blends can be improved by compounding with graphite.[287]

4.5.1.11 Oxidized polyethylene, OPE

Oxidized polyethylene is a common lubricant and fusion promoter.[268,288] Oxidation reaction occurs at chain ends and points of branching, or at infrequent sites of unsaturation. It creates polarity and compatibility with PVC. A typical OPE used in PVC has medium

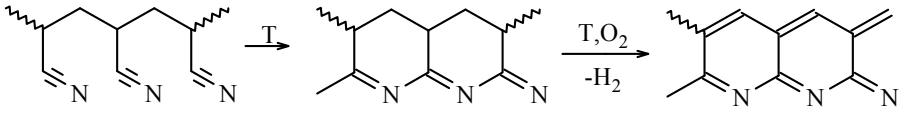
density (M_w 2,000-4,000) and low oxidation (acid number 6-20).[268] Being an external lubricant, OPE is expected to delay the fusion of PVC, but in combination with calcium stearate it accelerates the fusion time.[268] Because it contains unsaturated bonds it is likely to increase degradation rate of PVC, but since it is added in very small concentrations (usually 0.3%), its effect on degradation was not noticed.

4.5.1.12 Polyacrylate

Polyacrylates are often added to rigid PVC as impact modifiers and processing aids. Efficient impact modifiers should be immiscible with the host polymer to form discrete domains, but they should also have a strong interfacial bonding to the matrix to permit good stress transfer across the interface. If the impact modifier becomes too compatible, impact modification will not occur. If the modifier becomes too incompatible, the compound loses its toughness.[275] Polyacrylates have gained a predominant position among PVC impact modifiers in profile and sheet extrusion.[289] The increased thermal stability of PVC with higher percentages of PEA were confirmed by TG and DSC studies.[290] The increase thermal stability in blend is explained by HCl scavenging ability of PEA, which decreases probability of autocatalysis by HCl.[290]

4.5.1.13 Polyacrylonitrile

According to Starnes,[26] polymers containing nitrile groups (nitrile rubber and polyacrylonitrile) destabilize PVC because of the retarded diffusion of HCl, caused by interaction of HCl with the nitrile substituents. Such an interaction is supposed to produce imine hydrochloride moieties, which are likely to be weaker catalysts than HCl itself.[26] At the same time it is known that polyacrylonitrile undergoes cyclization at fairly low temperatures.[291] The following mechanism of reaction leads to formation of polyimides:[291]



PAN polyimide highly conjugated structure

The highly conjugated structure is very stable. It does not undergo oxidation and it is unlikely to take part in any interaction with HCl which may influence dehydrochlorination rate of PVC. If there is an influence similar to NBR it will rather be limited by formation of conjugation. Data on PAN influence on dehydrochlorination rate cannot be found.

4.5.1.14 Polyamide

It is difficult to blend PVC with polyamides because of differences of processing temperatures and crystallinity. Still, PVC/polyamide blends were commercialized. Ethylene copolymers are used in these blends as compatibilizers. The ethylene copolymer is first blended with polyamide, then the binary blend is blended with PVC. These blends display an attractive combination of properties including flame resistance, toughness, chemical resistance, low-temperature flexibility, outstanding abrasion resistance, strength, and processability.[291] No data on thermal stability of these blends can be found.

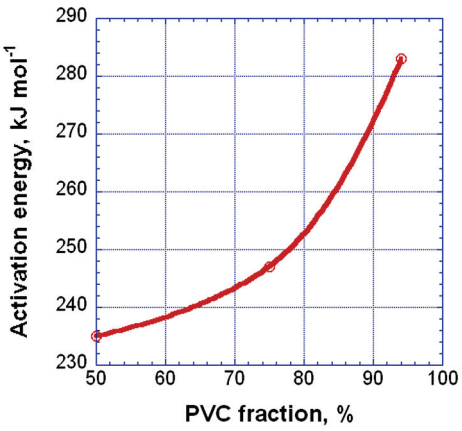


Figure 4.52. Activation energy of dehydrochlorination of PVC/PANI blends vs. PVC fraction. [Data from de Farias, R. F.; Nunes, L. M., *J. Thermal Anal. Calorimetry*, **70**, 559-564, 2002.]

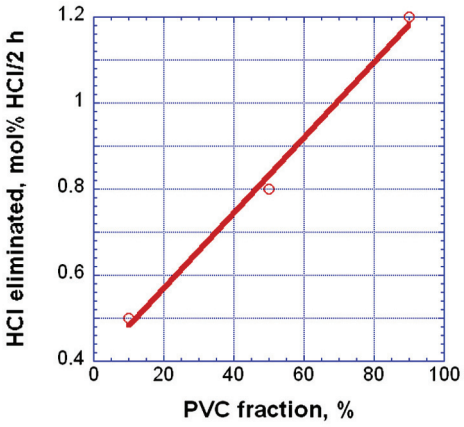


Figure 4.53. The amount of HCl eliminated from PVC/PC blends vs. PVC fraction in the blend. [Data from Braun, D.; Boehringer, B.; Eidam, N.; Fischer, M.; Koemmerling, S., *Angew. Makromol. Chem*., **216**, 3865, 1-19, 1994.]

4.5.1.15 Poly(ε-caprolactone), PCL

Blending PCL with PVC increases thermal stability of PVC.[292] Addition of montmorillonite further increases thermal stability of the blend.[292] PCL acts as internal plasticizer in blend with PVC.[293] Tin-containing compounds can be used as catalysts of caprolactone polymerization and then remaining catalyst acts as PVC thermal stabilizer.[293]

4.5.1.16 Polyaniline, PANI

Polyaniline is blended with PVC to obtain conductive blends.[294-296] Uniform looking composite films are insensitive to the heat treatment until 100°C. The small black spots gradually appear and grow in number.[294-295] Figure 4.52 shows that activation energy of dehydrochlorination decreases with polyaniline fraction increasing, which demonstrates that polyaniline destabilizes PVC.[296] It was found that some HCl produced in dehydrochlorination reaction is used internally for doping polyaniline.[294,295]

4.5.1.17 Polycarbonate, PC

PVC forms miscible blends with liquid crystalline PC[297] but forms immiscible blends with PC.[298] Figure 4.53 shows that the presence of poly(bispenol A) carbonate decreases dehydrochlorination rate by dilution. It should be noted that this is an isolated case because four other polycarbonates increased dehydrochlorination rate at their highest concentration (90% PC). The difference in behavior is explained[278] by glass transition temperature. Poly(bisphenol A) carbonate is the only polycarbonate tested which has glass transition temperature lower than PVC degradation temperature (180°C). The other polycarbonates having higher glass transition temperatures trap HCl for longer periods of time by which they prolong its catalytic influence on PVC dehydrochlorination.[278]

It is interesting to mention that PVC does not reciprocate inert behavior of PC and it affects PC stability in their blends. PC has a decomposition temperature of 503°C (as measured by thermogravimetry) if degraded alone but in PVC/PC blends PC degrades at 441°C.[296] The PVC case is opposite. It begins to degrade at 291°C when exposed to temperature alone but in the blend with PC it begins to degrade at 350°C. It was noticeable that the addition of only 10% PVC destabilized the blend. The destabilization is explained by participation of chlorine radicals in abstraction of hydrogen from PC, which causes its destabilization.[296]

4.5.1.18 Polyethylene, PE

Low molecular weight polyethylene wax is used as a lubricant[299] in PVC extrusion, especially in the production of pipes.[300-302] High molecular weight polymer forms immiscible blends with PVC.[287] According to the principles of polaron mechanism,[202] polyethylene is expected to reduce PVC dehydrochlorination but there is no experimental data which may support this prediction. Polyethylene wax is a good source of fuels and thus it increases smoke emission from PVC fire.[304]

4.5.1.19 Poly(ethylene oxide), PEO

Thermogravimetric analysis in dynamic and isothermal heating regime was used for studies of thermal stability of PVC/PEO blends.[305] PEO has greater thermal stability than PVC.[305] The degradation of blend is a two stage process.[305] In the first stage, PVC dehydrochlorinates.[305] In the second stage, degradation of both polymers occurs.[305] At higher than 20% concentrations, PEO stabilizes PVC.[305]

4.5.1.20 Poly(3-hydroxyalkanoate), PHA

Poly(3-hydroxyalkanoate) was used as eco-friendly PVC plasticizer.[306] PVC/PHA blend had lower thermal stability than unplasticized PVC.[306] All PVC/PHA blends had lower activation energy of degradation and entropy of activation for thermodegradation than PVC.[307] Higher reduction of both factors was observed when the proportion of PHA was increased in the blend; and when oligomeric PHA was used as the plasticizer instead of polymeric PHA.[307]

4.5.1.21 Poly(methyl methacrylate), PMMA

Poly(methyl methacrylate) and other methacrylates are used as process aids,[308] and they improve PVC stiffness and heat distortion.[309] There is no single answer regarding blend miscibility because it depends on conditions of its preparation. PMMA, poly(phenyl methacrylate), poly(cyclohexyl methacrylate), and poly(benzyl methacrylate) blends with PVC are immiscible[310] but there is research which shows that blends can be miscible, immiscible, or miscible in a certain range of concentrations of polymers.[311] This suggests the obvious conclusion that blend formation between PVC and PMMA is a complex process. It was found that syndiotactic PMMA is more miscible with PVC than isotactic PMMA. On the other hand, syndiotactic PVC is less miscible with PMMA than atactic PVC.[312] This shows that there are morphological constraints which affect miscibility. If information on morphological features of both polymers is not available, it is thus difficult to assess why some blends are miscible or immiscible. It is quite certain that PVC/PMMA blends can be

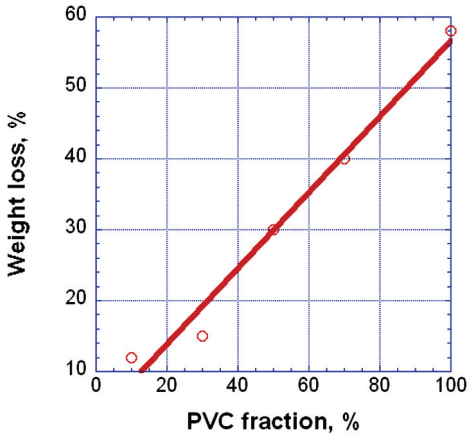


Figure 4.54. Weight loss of PVC/PMMA blend vs. PVC fraction in the blend. [Data from Belhaneche-Bensemra, N.; Bedda, A.; Belaabed, B., *Macromol. Symp.*, **202**, 151-165, 2003.]

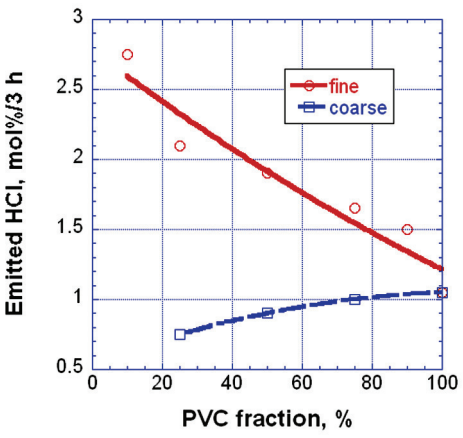


Figure 4.55. Amount of HCl emitted during 3 h of heating at 180°C under nitrogen. [Data from Braun, D.; Boehringer, B.; Knoll, W.; Eidam, N.; Mao, W., *Angew. Makromol. Chem.*, **181**, 2997, 23-39, 1990.]

made practically[275] and completely[313] miscible by reactive processing. Reactive processed blends had single phase morphology and single glass transition temperature.[313]

Acrylic process aids are beneficial in PVC processing because of their ability to promote fusion, increase melt strength, increase melt elasticity, and, for some particular grades, reduce sticking to metal parts.[314] These are essential parameters which affect duration of heat exposure but there are many other data characterizing thermal stability of PVC/PMMA blends.[278,308,315,316] Figure 4.54 shows that the weight loss is proportional to PVC concentration. Lowering weight loss in the first stage of blend degradation (dehydrochlorination) should be attributed to dilution of HCl producing polymer (PVC) by PMMA.[315] Blends showed miscibility up to 50 wt% PMMA. The miscibility was attributed to hydrogen bonding between carbonyl groups of PMMA and hydrogen of CHCl groups in PVC.[315]

Earlier studies show that thermal stability of PVC blends depends on the quality of mixing (Figure 4.55). In homogeneously mixed blends addition of PMMA decreases stability of PVC but coarse blends have increased stability.[308] This will suggest that in the coarse mixed blends HCl is absorbed in PMMA, which inhibits catalysis of dehydrochlorination. During this study, which included different methacrylates, it was found that all poly(methacry1ate)s have an influence on the degradation of PVC in blends. Longer n-alkylester groups and higher concentrations of the corresponding poly(methacry1ate) exhibit some stabilization of PVC, whereas smaller ester chains and low concentrations lead to destabilization.[308]

The thermal decomposition temperatures of the first and second stage of degradation in PVC in the blend with PMMA were higher than for pure PVC.[317] 10 wt% PMMA content in the PVC matrix gave the most significant stabilizing effect.[317]

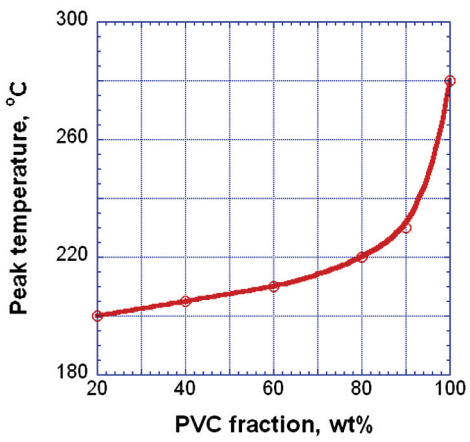


Figure 4.56. Peak temperature of dehydrochlorination of PVC/PVP blends vs. PVC fraction. [Data from Dong, J.; Fredericks, P. M.; George, G. A., *Polym. Deg. Stab*., **58**, 159-169, 1997.]

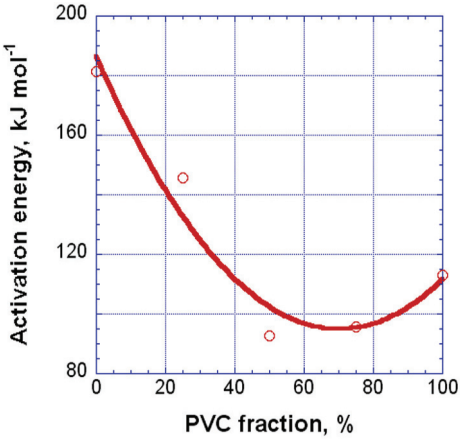


Figure 4.57. Activation energy of dehydrochlorination of PVC/poly(diphenyl siloxane) vs. PVC fraction. [Data from Zulfiqar, S.; Ahmad, S., *Polym. Deg. Stab*., **65**, 2, 243-247, 1999.]

4.5.1.22 Poly(N-vinyl-2-pyrrolidone), PVP

Poly(N-vinyl-2-pyrrolidone) forms miscible blends with PVC.[318] Figure 4.56 shows that addition of PVP decreases thermal stability of PVC in the blend measured by the temperature of the dehydrochlorination peak.[318] It is proposed by authors[318] that dehydrochlorination is either catalyzed by the presence of carbonyl groups or by tertiary amide groups.

4.5.1.23 Polysiloxane

Figure 4.57 shows that activation energy of degradation of PVC polysiloxane blends increases with the amount of polysiloxane in the blend.[319] Figure 4.57 also shows that polysiloxanes are substantially more stable than PVC. Improved stability of the blend is more noticeable when concentration of polysiloxane is at least 50%. It is speculated that the improvement of PVC thermal stability is caused by absorption of HCl into polysiloxane phase which reduces its catalytic influence on PVC thermal degradation.[319]

4.5.1.24 Polystyrene, PS

Figure 4.58 shows the effect of addition of PS on thermal stability of PVC blend. PS decreases PVC dehydrochlorination more extensively as would be expected from dilution of degrading polymer (PVC).[316] The influence of PS on thermal stability of PVC is explained by diffusion of HCl into PS phase (removal of catalyst from PVC) and lowering polarity, which also decreases the rate of HCl loss.[316] In earlier studies,[260] PS was also found to decrease PVC degradation but HIPS increased PVC degradation rate (see Figure 4.49 and Section 4.5.1.6). Activation energy of the degradation was increased with the addition of a small amount of PVC in PS.[321] The stabilization effect on PS depends on the heating rate and the blend composition.[321] Also, reduction in pyrolysis products was observed.[321]

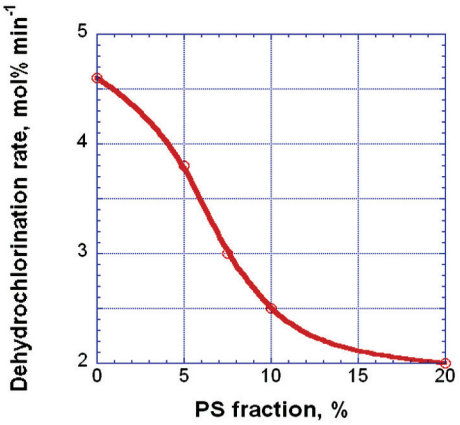


Figure 4.58. Dehydrochlorination rate of PVC in PVC/PS blend vs. PS fraction. [Data from Yao, Q.; Wilkie, C. A., *J. Vinyl Additive Technol.*, **7**, 1, 26-36, 2001.]

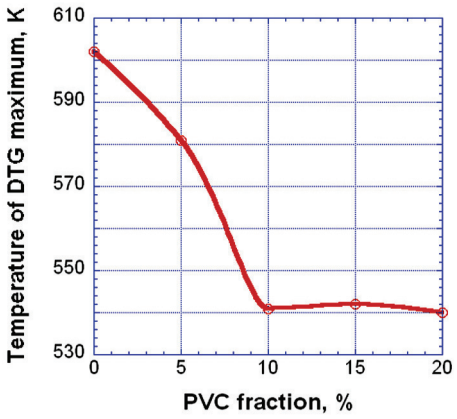


Figure 4.59. Temperature of DTG maximum vs. PVC fraction. [Data from Pielichowski, K.; Janowski, B., *J. Thermal Anal. Calorimetry*, **80**, 1, 147-151, 2005.]

Blending PVC with PS slightly increased benzene formation during PVC thermal degradation under nitrogen.[316] Addition of PVC to PS increases its fire retardancy and heat release rate from PS during burning.[316] Incineration of mixture PVC+PS substantially reduces the amount of toxic gases which are produced during incineration (polychlorinated dibenzodioxins, polychlorinated dibenzofurans, and polychlorinated biphenyls).[320] From the extent of reduction in produced toxic gases it is clear that the presence of PS changes the mechanism of pyrolysis.

4.5.1.25 Polythiophene

Ternary blends (PEO/PEDOT-PSS/PVC) were studied.[322] It was observed that the presence of PEDOT-PSS in the binary blends did not change the thermal stability but the stability was improved by PEO.[322]

4.5.1.26 Polyurethane

PVC was found to be miscible with aliphatic polyester segment.[323] Phase separated hard-block acted as the physical crosslinking of the blend. If hard segment concentration was increased, the miscibility of PVC/PU blends was decreased.[324]

Figure 4.59 shows that even a small addition of PVC into PVC/PU blend destabilizes PU. This is confirmed by another study[275] which shows that PU increases stability of PVC. On the other hand, PVC makes PU less flammable.

Studies were made on the effect of PU foam backing on thermal stability of PVC.[326,327] It was concluded that the reason for more extensive PVC degradation at the foam surface is attributable to additives used in the foam preparation (e.g., catalyst, diethylenetriamine).[326] Polyenes were longer at the areas of contacts between foam and PVC film than in the area of PVC contact with air.[327]

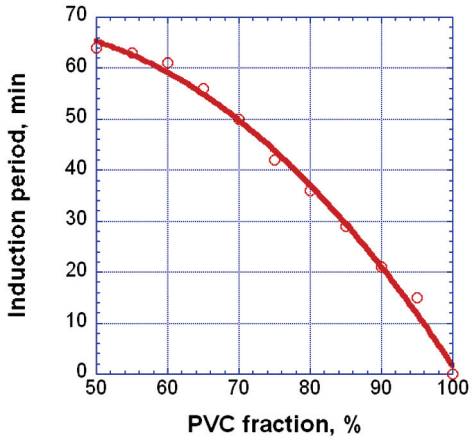


Figure 4.60. Induction period of PVC/PVB blend degradation vs. PVC fraction. [Data from Mohamed, N. A.; Sabaa, M. W., *Eur. Polym. J.*, **35**, 9, 1731-1737, 1999.]

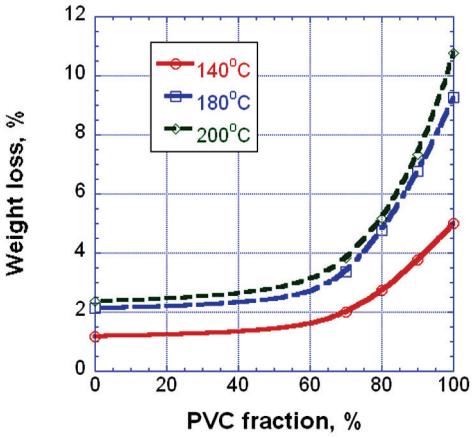


Figure 4.61. Weight loss during degradation of PVC/PVB blend vs. PVC fraction for different degradation temperatures. [Data from Mohamed, N. A.; Sabaa, M. W., *Eur. Polym. J.*, **35**, 9, 1731-1737, 1999.]

4.5.1.27 Poly(vinyl acetate), PVAc

PVAc is known to be more stable than PVC (activation energy of thermal degradation of PVAc is 215 kJ mol^{-1} and PVC is in the range from 126 to 130 kJ mol^{-1}).[11] The PVC/PVAc blends are less stable at lower temperatures but they have better stability at higher temperatures.[328] The poorer initial stability is explained by the mutual catalytic effect of degradation products of both polymers (hydrogen chloride catalyzes the loss of acetic acid from PVAc and acetic acid catalyzes the loss of hydrogen chloride from PVC).[328] Better stability of blends at higher temperatures is due to contribution of the conjugated structure which may serve as a "radical sink" for radicals involved in the degradation.

4.5.1.28 Poly(vinyl alcohol), PVA

PVA is commonly used in PVC polymerization as a protective colloid.[38] It controls PVC porosity and grain size. PVA is less thermally stable than PVC (activation energy of thermal degradation of PVA is in the range of 61.1 to 97.9 kJ mol^{-1}).[11] There is no data available on its influence on PVC thermal degradation. Partially saponified polyvinyl alcohol having a low degree of polymerization and a medium degree of hydrolysis improves the thermal stability of PVC mixtures stabilized with metal ions.[329] PVC Contains less than 5% PVA having degree of saponification from 75 to 99.9 mol% and degree of polymerization of 450 or less.[330] The blend contains also zinc compound as stabilizer.[330] Such compound has excellent thermal stability.[330]

4.5.1.29 Poly(vinyl butyral), PVB

PVB is most commonly known for its application as an interlayer polymer in safety glass manufacture but it is also used as an impact modifier for PVC.[331] Figure 4.60 shows that addition of PVB helps to increase stability of PVC/PVB blend. Also, weight loss during thermogravimetric measurements at different temperatures shows that thermal stability of

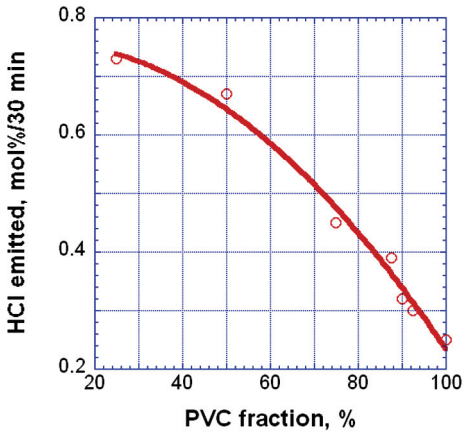


Figure 4.62. HCl emitted vs. PVC fraction in PVC/SAN blend. [Data from Kuzelova, K.; Vymazal, Z., *Eur. Polym. J.*, **35**, 2, 361-364, 1998.]

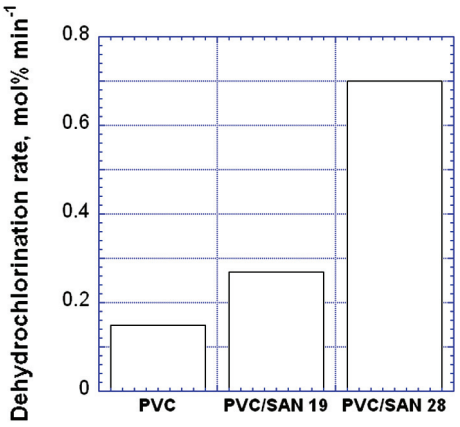


Figure 4.63. Dehydrochlorination rate of PVC and its blends. [Data from Braun, D.; Boehringer, B.; Eidam, N.; Fischer, M.; Koemmerling, S., *Angew. Makromol. Chem.*, **216**, 3865, 1-19, 1994.]

blend is improved by PVB (Figure 4.61).[332] The authors of the data explain the improvement of thermal stability by substitution of labile chlorines in PVC by a more stable ester group.[332] It is clear from the data that dilution does not explain the dramatic improvement. Also, the authors explanation does not cover the entire extent of improvement because even at high concentration of PVB, thermal stability of blend improves, which would not occur if substitution would have been the only reason in addition to dilution, because concentration of labile chlorines is very small compared to the amount of ester groups added with PVB.

4.5.1.30 SAN

SAN forms immiscible blends with PVC. Figure 4.62 shows that SAN increases PVC degradation rate.[333] Authors, following studies on PVC/NBR blends, suggest that increased degradation rate is caused by formation of CN...HCl complex which accelerates dehydrochlorination. Indeed, Figure 4.63 shows that addition of SAN to blend increases its dehydrochlorination.[278] The dehydrochlorination rate increases more for blend with SAN 28 (28% acrylonitrile) than for blend with SAN 19 (19% acrylonitrile). Braun *et al*.[278] suggested that the above mentioned interaction may retard diffusion of HCl and thus increase duration of its catalytic activity.

4.5.2 ANTIBLOCKING

The antiblocking (aluminosilicate, natural silica, and synthetic silica), release (ethylene N,N'-bis-stearamide, ester wax, and glycerol monostearate), and slip agents (ethylene N,N'-bis-oleamide, stearamide, Zn and/or Ca stearate) are known to be used in PVC.[334] Out of these, the influence on thermal degradation of PVC of Zn/Ca stearates is known because they are thermal stabilizers of PVC).

4.5.3 ANTISTATICS AGENTS

Antistatics used in PVC include: carbon black, chlorinated polyethylene, conductive polymers (see section 4.5.1), copper powder, dimethylethyl soya ammonium ethosulfate, 1-dodecylpyridinium chloride monohydrate, ethoxylated fatty dimethyl ethylammoniumethosulfate, ethylene oxide condensate, fluorinated alkyl polyoxyethylene ethanol, glycerol monostearate, graphite, lauric diethanol amide, poly(ethylene oxide), polyethylene glycol monolaurate, propanesultone, and sodium sec-alkane sulfonate.[335] The effect on thermal stability of PVC was studied for only a few additives on the list. It was found[336] that glycerine ester derivative, graphite, metal powder (copper), and metal oxide (antimony oxide and tin oxide) did not affect color change on exposure to 200°C. Some of them (graphite and copper) affected initial color.

In the past, various surface active agents, migrating to the surface, were used as antistatic agents. Some of them are still on the list of applicable additives. Figure 4.64 shows that both antistatic additives increase the rate of PVC dehydrochlorination but ionic surface active agents have stronger influence on PVC thermal stability.[49]

4.5.4 BIOCIDES AND FUNGICIDES

10,10-oxybisphenoxarsine (OBPA), zinc pyrithione (ZnP), 2-n-octyl-isothiazolin-3-one (OIT), 4,5-dichloro-2-n-octylisothiazolin-3-one (DCOIT), chlortalonil (CTHL), and N-dichlorofluoromethylthiophthalimide, Fluorfolpet (FF) are examples of biocides and fungicides used in PVC.[337-340] Out of these, only ZnP was tested for its influence on PVC thermal degradation and it was found[340] that it affects change of color of PVC formulation (Figure 4.65). In both cases, degradation of initial color occurs very rapidly when it begins but degradation begins almost 3 times faster in the presence of biocide.[340] There are no data on the influence of other biocides/fungicides in spite of the fact that some of them have been in use for almost half a century. Baerlocher developed Baerostab UBZ 635 XLP RF and Baerostab UBZ 782 XLP RF for use with biocide dichloro-n-octyl-isothiazolinone.[343] These products do not produce undesirable reactions with biocide and thus improve stabilization of PVC.[343] A thermostable, arsenic-free biocide concentrate composition comprising at least one biocide selected from trihalomethyl-thiophthalimide and antioxidant which permit processing in temperatures up to 250°C.[344]

4.5.5 BLOWING AGENTS

The two main blowing agents used in the production of rigid WC foam are azodicarbonamide (ADC) and sodium bicarbonate (SBC).[341,342] Nitrogen is the major gaseous product of ADC decomposition. Other products are CO_2, CO and NH_3.[342] SBC produces on its decomposition CO_2 and H_2O. SBS is an endothermic blowing agent (absorbs heat) and ADC is an exothermic blowing agent (produces heat while decomposing). In addition to

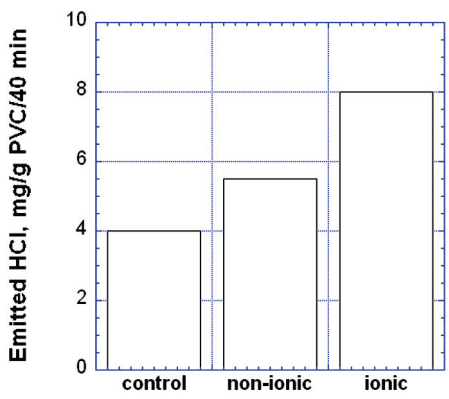


Figure 4.64. Effect of antistatic additives on PVC dehydrochlorination. [Data from Wypych, J., *Angew. Makromol. Chem*., **48**, 654, 1-15, 1975.]

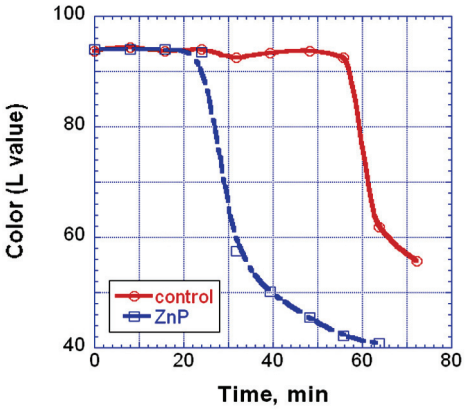


Figure 4.65. Color change vs. time of oven heating at 190oC. [Data from Burley, J. W.; Clifford, P. D., *J. Vinyl Additive Technol.*, **10**, 2, 95-98, 2004.]

blowing agents, the so-called kickers are used to regulate their decomposition temperature (and thus rate of decomposition of the blowing agent). These kickers usually have PVC-stabilizing properties. Information on the effect of blowing agents on PVC thermal stability cannot be found in open literature.

4.5.6 FILLERS

Aluminum fiber, aluminum hydroxide, antimony trioxide, calcium carbonate, carbon fiber, clay, hollow glass beads, kaolin, magnesium hydroxide, mica, sand, silica (including nano-silica), silicon carbide, talc, waste leather particles, wollastonite, and wood fiber and flour are the major fillers used in PVC.[345-355] These fillers are known to reduce thermal stability of PVC: copper-containing compounds, iron salts, cadmium, cobalt, manganese, lead salts (also other fillers containing these metals).[345] It is noticeable that degrading fillers are not on the list of common fillers.

Fillers are also added to PVC to provide thermal stabilization. For example, calcium stearate may play the role of an associate thermal stabilizer when used in a system with calcium salts of fatty acids. These stabilizers use combinations of two or more metals, one of which (e.g., zinc) produces metal chlorides which accelerate PVC degradation. The presence of a large amount of calcium salt helps to convert this chloride to calcium chloride, which does not increase the degradation rate of PVC. Also, calcium carbonate can react with hydrogen chloride which is produced as PVC degrades. Braun and Kraemer[356] proposed to use addition of calcium carbonate in PVC recycling. Addition of 10% chalk is sufficient to improve stability of PVC for repeated processing (Figure 4.66).[31,356] Calcium carbonate the nanoparticles were modified with poly(acrylic acid) and poly(butadiene-co-acrylonitrile-co-acrylic acid).[358] The gelation time decreased as a function of the percentage and surface treatment of $CaCO_3$.[358] A significant improvement in the PVC thermal stability was noted with the addition of neat and stearic acid modified $CaCO_3$.[358] Thermal properties of PVC/$CaCO_3$ nanocomposites were better than commercial filled $CaCO_3$

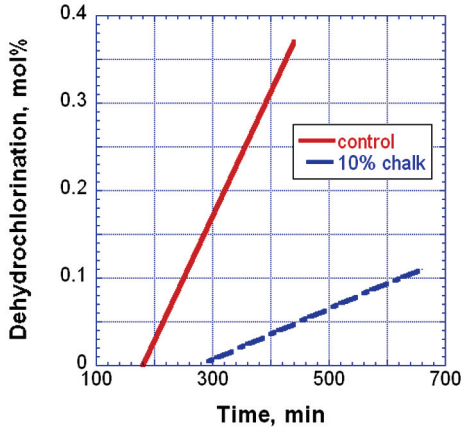


Figure 4.66. Dehydrochlorination rate of PVC with and without 10% calcium carbonate. [Adapted, by permission, from Braun D.; Kraemer K., **Recycling of PVC & Mixed Plastic Waste**, La Mantia F. P, Ed., *ChemTec Publishing*, Toronto, 1996.]

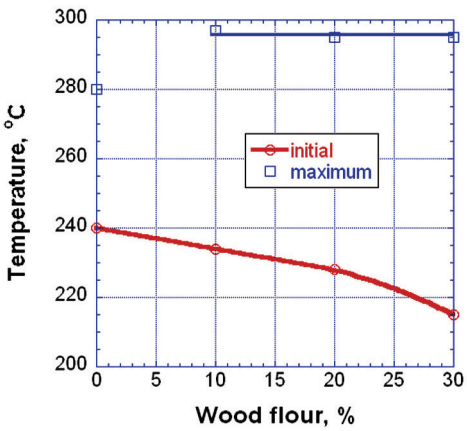


Figure 4.67. Temperature of weight loss beginning and temperature of maximum weight loss vs. wood flour content. [Data from Djidjelli, H.; Martinez-Vega, J.-J.; Farenc, J.; Benachour, D., *Macromol. Mater. Eng.*, **287**, 9, 611-618, 2002.]

PVC composites.[360] Synergistic stabilizing effect was observed for compositions including nano-$CaCO_3$ and layered double hydroxides.[361]

When wood flour is used as a filler, degradation begins at lower temperature[357,359] when the content of wood flour increases but maximum degradation temperature is constant for each tested wood flour content and higher than for control (Figure 4.67). Wood flour retarded thermal decomposition at early stages and promoted crosslinking and charring reactions.[357,359,362] Addition of wood flour also decreased average heat release rate and its peak.[359]

It was also discovered that the particle size of filler may have some influence on the degradation process. In the case reported in Figure 4.68, fusion time increases with particle size increasing.[355] Longer fusion time means longer exposure to heat, which must be compensated by adequate stabilization.

Montmorillonite was intercalated with different organic intercalants.[363] Cationic intercalants were found to accelerate the dehydrochlorination of PVC whereas the non-ionic did not affect thermal degradation.[363]

Analysis of the above information permits us to conclude that there are fillers which may accelerate PVC thermal degradation, but in modern technology these fillers are known and they are not used in PVC processing. Fillers in typical use have either no effect on PVC thermal degradation process or give some improvement, as in the example given for calcium carbonate.

4.5.7 FLAME RETARDANTS

Numerous flame retarding materials are used in PVC or are under research.[208,241,242,300,364-378] Metals involved include Al, Cu, Fe, Mg, Mo, Sb, Sn, Zn. Their oxides (hydroxides) and frequently chlorides are suitable candidates for flame retardants

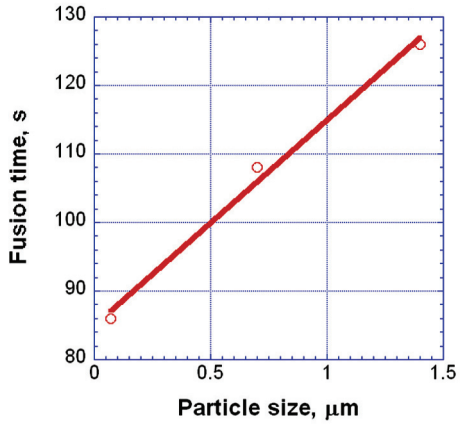


Figure. 4.68. Fusion time of PVC formulation containing $CaCO_3$ at temperature 155°C vs. particle size of filler. [Data from Azimipour, B.; Marchand, F., *J. Vinyl Additive Technol*., **12**, 2, 55-57, 2006.]

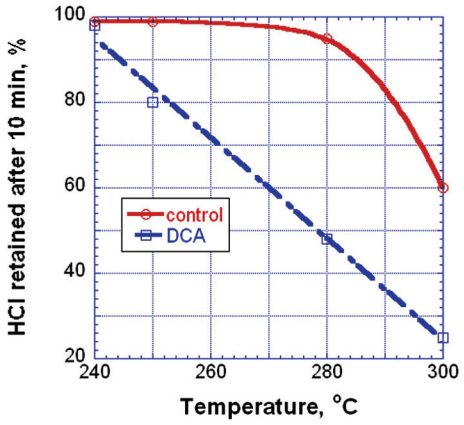


Figure 4.69. HCl retained after 10 min of heating vs. heating temperature for formulation with and without chlorinated aromatic acid derivative (DCA). [Data from Carty, P.; Grant, J.; Metcalfe, E., *Appl. Organometallic Chem.*, **10**, 2, 101-11, 1996.]

and smoke suppressants. Also, many organic materials are used including ferrocene derivatives,[242,365] phosphoric acid esters (flame retardant plasticizers),[366,368,371] polyphosphate plasticizers,[368] polyethylene stybnite phosphate esters,[369] chlorinated paraffins,[208,366] brominated plasticizers,[208] hexachloropentadiene,[373] dienofiles,[373] and ammonium sulfamate.[374] The most popular are antimony oxide, aluminum trihydrate, magnesium hydroxide, phosphate plasticizers, zinc borate,[357] copper compounds (char formers), and molybdenum-based smoke suppressants.[366]

Most flame retardants decrease PVC thermal stability because their mechanism of action involves making use of HCl for fire retarding capabilities. For example, addition of Sb_2O_3 and SnO_2 decreases activation energy of the first stage degradation (mainly dehydrochlorination) from 91.5 kJ mol^{-1} for PVC without flame retardants to 58.7 and 47.7 kJ mol^{-1}, respectively.[364] Metal chelates decrease degradation temperature of PVC.[241] Zn hydroxystannate and Zn stannate decreased the beginning temperature of the first stage degradation by 13 to 38°C.[300,375] Zinc hydroxystannate promotes crosslinking and catalyzes dehydrochlorination.[375] HCl acts as a blowing agent enhancing intumescent properties of material.[375]

In application of various ferrocene derivatives, it was found that the most effective flame retardants (chlorinated (DCA) and brominated (PBA) aromatic amide derivatives) reduced activation energy of dehydrochlorination (see Figure 4.69) but the best smoke suppressant (dichlorobenzoyl ferrocene (DCBF) did not affect dehydrochlorination rate. Also, activation energy of dehydrochlorination was reduced with ferrocene derivatives.[242] For PVC without ferrocenes it was 90 kJ mol^{-1} and it was decreased to 35 for PBA, 75 for DCA, and only to 85 kJ mol^{-1} for DCBF.[242]

Zinc borate did not affect initial temperature of PVC degradation but later rapidly increased degradation rate.[357] Zinc borate promoted crosslinking and charring reactions.[357]

4.5.8 IMPACT MODIFIERS

Section 4.5.1 contains information on various polymer pairs – some of which are used for impact modification.

4.5.9 LUBRICANTS

A wide range of lubricants are used in PVC,[264,268,314,379-386] including acrylic process aids (affect lubrication),[386] amide waxes,[380] fatty acids and their esters,[264,383] glycerol monostearate,[386] metal carboxylates (also thermal stabilizers),[379] N,N-diacyl ethylenediamine,[381] N,N'-ethylene bis-stearamide,[264] oxidized polyethylene,[268] and paraffin wax.[382] Stearic acid is the most popular PVC lubricant. The nature of lubricants suggests that they unlikely directly affect PVC stability but they have many influences which impact PVC degradation. Rheological studies permitted separation of heat flow from the wall and heat generated by the extruder screw to assess the influence of lubricants on heat generation process and thus thermal stability of PVC formulations.[385] This development underlines one of the influences of lubricants on PVC degradation. Lubricants also affect fusion time and temperature, which influences material exposure to heat. External lubricants generally delay fusion and internal lubricants shorten fusion time (this rule is not always precise).[268] Finally, lubricants may separate from melt at elevated temperatures and form a defect within material which may affect mechanical performance of the material.[382]

In summary, lubricant selection has many direct and indirect influences on PVC thermal stability and it should be considered in conjunction with the selected stabilizing system, considering that some stabilizers have also lubricating properties.

4.5.10 PIGMENTS

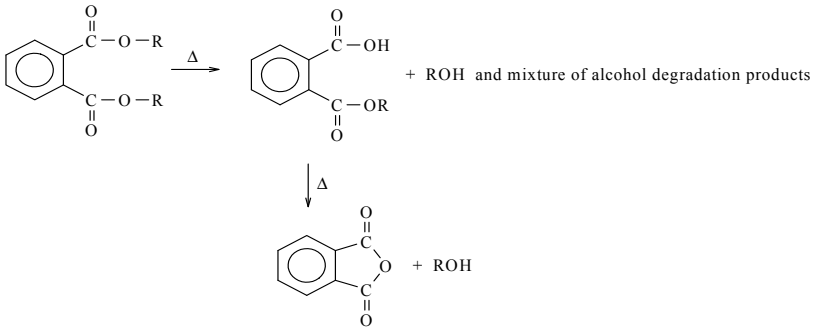
A wide variety of inorganic and organic pigments is used in PVC but information on their effect on PVC thermal degradation is limited. The only direct influence on thermal degradation is related to the effect of iron oxides which are known to increase PVC degradation rate.[387] Also, some grades of carbon black used in production of video disks caused melt instability. [387] Surface oxygen had the greatest effect on this instability. It was confirmed by experimental studies that TiO_2 and some other pigments may influence fusion characteristics and melt rheology.[302] A color shift was observed when some red anthraquinone pigments were used. Materials were changing color during warehousing even though they were not exposed to light.[352] Studies revealed that this only happened when TiO_2 exceeded 88% of total color package. Larger concentrations of TiO_2 increased crystallization in the system which reduced solubility of organic pigments and this has produced a bathochromic shift.[388]

This very limited information shows an urgent need for further studies. It is true that pigment manufacturers test pigments prior to introduction but pigments are used in combination and in complex formulation which may affect pigment and polymer performance. The best remedy for such a situation is fundamental knowledge which is clearly not available.

4.5.11 PLASTICIZERS

A very large number of different plasticizers are used in PVC. They belong to the following groups: abietates, adipates, azelates, benzoates, chlorinated paraffins, citrates, glycol ethers and their esters, pentaerythritol derivatives, phosphates, phthalates, polymeric, sebacates, trimellitates, pyromellitates, and many application-specific plasticizers. Full information about plasticizers and plasticization can be found in specialized publications.[389,390]

There are many ways in which plasticizer may influence thermal degradation. One is related to plasticizer degradation:



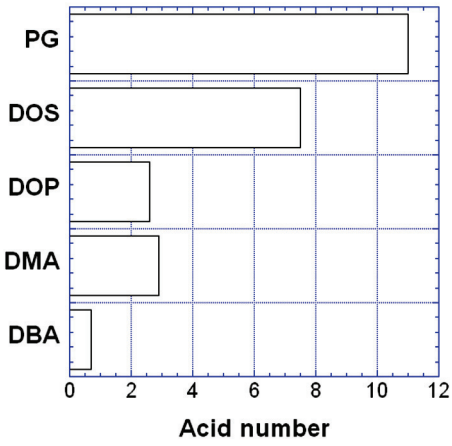


Figure 4.70. Acid number of PVC dry blends heated at 170°C for 90 min. Formulation PVC 100, plasticizer 40, barium stearate 1.5, calcium stearate 1.5. PG polyester based on thriethylene glycol. [Data from Barshtein R S, *Plastmassy*, 12, 13-15, 1968.]

Phthalic acid, for example, decomposes at 230°C to phthalic anhydride but many alcohols have boiling points well below this temperature.[390] Decomposition is partially due to increased temperature but mostly due to the presence of HCl which can hydrolyze plasticizers. Figure 4.70 illustrates potential changes with different plasticizers. Figure 4.71 shows that acids formed *in situ* in PVC formulation affect dehydrochlorination rate expressed by thermostability number A.[392,393] The higher the thermostability number A, the more stable the test formulation. The higher the pK_1 of acid, the more stable formulation. Note that most of these acids (all except stearic) are polyprotic acids and thus they have two constants characterizing their dissociation. The second constant, pK_2, is very similar for dicarboxylic acids (adipic acid – 5.41, glutaric acid – 5.42, phthalic acid – 5.43, heptanedioic acid – 5.58, and sebacic acid – 5.59). The elimination of the second alcohol rest has a similar influence as liberation of the first carboxylic group. In the case of phosphoric acid, there are three

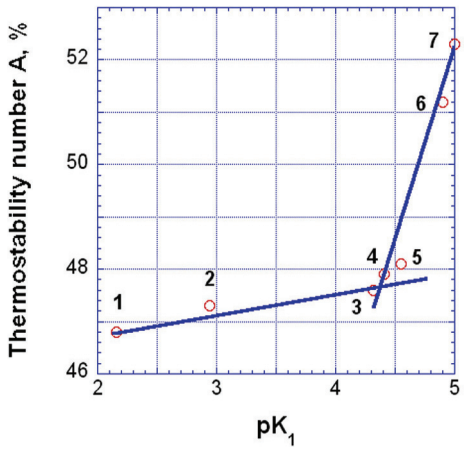


Figure 4.71. Thermostability number A of PVC film vs. pK_1 of acid added to formulation. Formulation: PVC 100 phr, DOP 60 phr, acid 2 phr. Acids: 1 - phosphoric, 2 - phthalic, 3 - glutaric, 4 - adipic, 5 - heptanedioic, 6 - sebacic, 7 - stearic. [Adapted, by permission, from Wypych, G., **Selected Properties of PVC Plastisols**, *Wroclaw University Press*, Wroclaw, 1977.]

constants involved: $pK_1 - 2.16$, $pK_2 - 7.12$, and $pK_3 - 12.32$.

It is well-established in organic chemistry that acids increase rates of halogen elimination. There is still no agreement as to the mechanism of thermal dehydrochlorination of PVC but ionic mechanisms prevail in disputes.

Loss of plasticizer due to the above discussed decomposition reaction and evaporation depends on:

- plasticizer type and concentration
- heating rate
- polymer-plasticizer interaction
- sequence of events in PVC thermal degradation.

Thermogravimetric analysis provides information on loss of mass which may be a result of degradation with volatilization of plasticizer component, plasticizer evaporation, or degradation and volatilization of any other component of the tested formulation (most likely polymer and stabilizer, because test formulations are usually kept simple). Because of these different reasons for mass loss, the results are difficult to interpret. In some studies, evaporation loss of plasticizer was distinguished from loss of degradation products by running two separate tests: one for the pure plasticizer and the other for the entire composition. This may help to better understand reasons for mass loss but the experiment changes conditions because products of plasticizer degradation affect degradation rate of polymer and degradation products of polymer affect degradation of plasticizers as previously discussed.

The rate of plasticizer loss corresponds to the molecular weight of the plasticizer. Several theoretical models were used to determine the best method of data interpretation and prediction of loss rate. It was found that the following relationship is useful for the analysis of data on plasticizer loss:

$$\frac{M_\tau}{M_0} = k\tau^d \qquad [4.17]$$

where:

M_τ plasticizer lost during time τ,
M_0 initial plasticizer content,
k k rate of loss,
τ time,
d constant (under experimental conditions d = 0.5).

The relationship between coefficient k and molecular mass is described by the following formula:[171]

$$\log k = 1 - 0.0062M \qquad [4.18]$$

where:

M molecular weight of plasticizer.

It has to be pointed out that the plasticizer loss occurs at any temperature and it is substantial at temperatures well below the boiling point of the plasticizer.

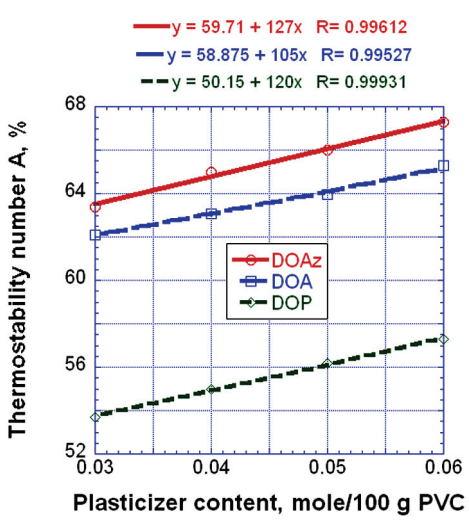


Figure 4.72. Effect of plasticizer type and content on thermostability of PVC plastificate containing: PVC 100 g, plasticizer - 0.03 to 0.06 moles. DOAz - dioctyl azelate, DOA - dioctyl adipate, DOP - dioctyl phthalate. [Adapted, by permission, from Wypych G, **Selected Properties of PVC Plastisols**, *Wroclaw University Press*, Wroclaw, 1977.]

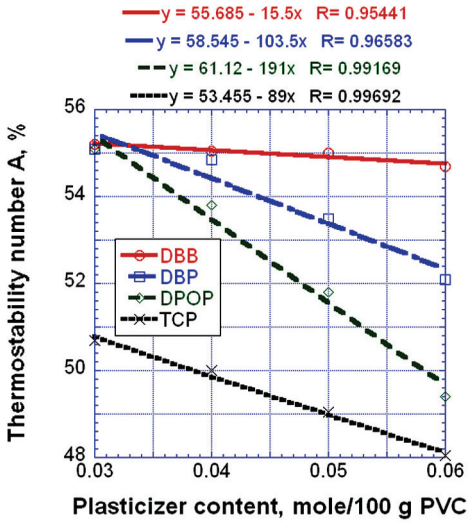


Figure 4.73. Effect of plasticizer type and content on thermostability of PVC plastificate containing: PVC 100 g, plasticizer - 0.03 to 0.06 moles. DBB - benzyl butyl phthalate, DBP - dibutyl phthalate, DPOP - diphenyl octyl phosphate, TCP - tricresyl phosphate. [Adapted, by permission, from Wypych G, **Selected Properties of PVC Plastisols**, *Wroclaw University Press*, Wroclaw, 1977.]

Figures 4.72 and 4.73 show that the effect of plasticizer concentration increase cannot be described by a simple relationship. Some plasticizers (e.g., dioctyl azelate, dioctyl adipate, and dioctyl phthalate) increase stability of PVC composition when their concentrations increase and other plasticizers (e.g., benzyl butyl phthalate, dibutyl phthalate, diphenyl octyl phosphate, and tricresyl phosphate) decrease stability of plastificate when their concentration increases. Both groups display linear relationships with good correlation coefficients. Comparing two groups of plasticizers, one may postulate that the group which increases stability of PVC contains less aggressive plasticizers than the group which decreases PVC stability.

In order to better understand these data, the results of thermostability testing are compared with dielectric constant, ε, polar cohesion energy solubility parameter of Hansen's scale, δ_P, and solution temperature determined according to DIN 53408. The resultant plots are given in Figures 4.74, 4.75, and 4.76, respectively. In all three plots a good correlation was obtained. Figure 4.74 shows that the plastisol thermostability decreases

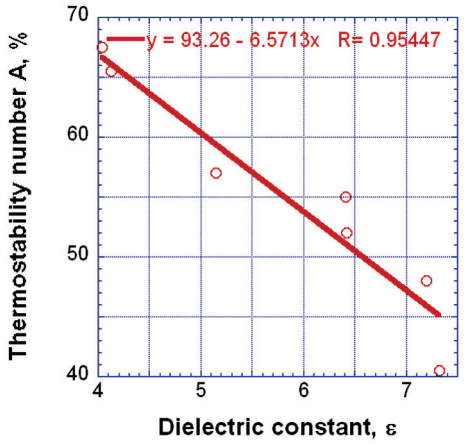


Figure 4.74. Thermostability number A from Figures 4.72 and 4.73 for 0.06 M plasticizer vs. dielectric constants of plasticizers. [Adapted, by permission, from Wypych, G., **Handbook of Plasticizers**, *ChemTec Publishing*, Toronto, 2012.]

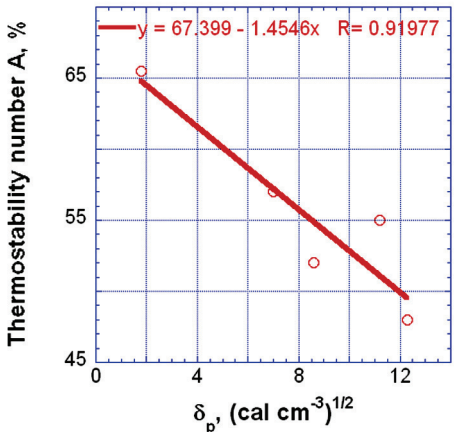


Figure 4.75. Thermostability number A from Figures 4.72 and 4.73 for 0.06 M plasticizer vs. cohesion energy solubility parameter of Hansen's scale of plasticizers. [Adapted, by permission, from Wypych, G., **Handbook of Plasticizers**, *ChemTec Publishing*, Toronto, 2012.]

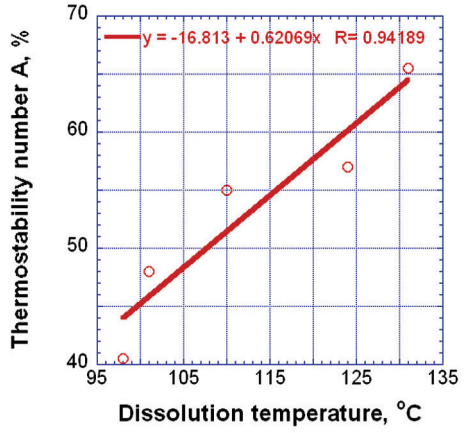


Figure 4.76. Thermostability number A from Figures 4.72 and 4.73 for 0.06 M plasticizer vs. dissolution temperature determined according to DIN 53408. [Dissolution temperatures from Polymer Additives. Plasticizers, Bayer SP-PMA 8013 E, 2000.] [Adapted, by permission, from Wypych, G., **Handbook of Plasticizers**, *ChemTec Publishing*, Toronto, 2012.]

with increase in dielectric constant of plasticizer. Figure 4.75 confirms that dielectric constant is a measure of solvent polarity. Increased polarity of plasticizer affects ionic polarization and increases probability of dehydrochlorination. Figure 4.76 shows that plasticizers which have better gelation abilities also cause more degradation.

From the data presented above, a complex relationship emerges which results from the existence of two types of relationships (Figures 4.72 and 4.73) caused by two competing influences:

- diluting effect of plasticizer which decreases probability of dehydrochlorination
- ionic polarization, and related to it, increased probability of HCl splitting off.

The above data clearly explain principles of influence of plasticizers on the PVC thermal degradation. The kinetics of these influences depends on the combination of the above discussed parameters which determine particular influences.

The above discussion on the influence of plasticizers is based on data presented by this author in 1970s publications[49,50,76,77,392,393] with some new correlations (Figures 4.74 to 4.76) published in the monograph on plasticizers.[390] The literature on the subject published after the 1970s is not very extensive[92,160,394-400] and the findings related to this discussion are reported below.

Marcilla and Beltran[400] compared temperatures to 50% weight loss for some phthalate and adipate plasticizers alone and the same plasticizers in the PVC formulation. The data shows that temperatures to 50% weight loss of a plasticizers dispersed in PVC are higher by only 2-14°C (in most cases 2-4°C) than temperatures to 50% weight loss when plasticizer was tested alone by the same thermogravimetric method.[400] This suggests that the loss of plasticizer is the first step of PVC thermal degradation. All plasticizers studied decreased thermal stability of PVC (measured by a temperature to 50% weight loss of total plastisol which was lower by 8 to 28°C than degradation of PVC without stabilizer). Considering that all data come from thermogravimetry, it is difficult to conclude whether it is because HCl accelerates degradation of plasticizer and thus increases its loss from the formulation or because the presence of plasticizer increases PVC thermal degradation and loss of mass is due to HCl emissions. But general observation for plastisols is that incorporation of phthalate or adipate plasticizer increases its mass loss.

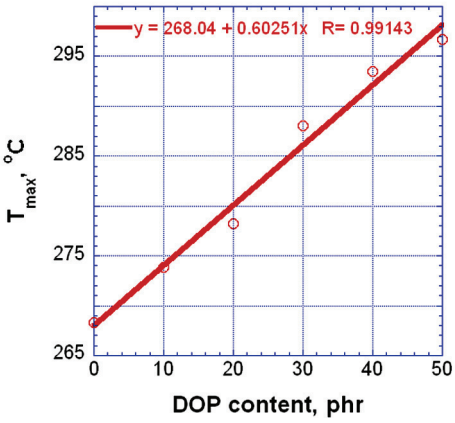


Figure 4.77. Maximum temperature of mass loss during thermogravimetric studies of PVC formations containing variable quantities of DOP. [Data from Djidjelli, H.; Sadoun, T.; Benachour, D., *J. Appl. Polym. Sci.*, **78**, 3, 685-691, 2000.]

Djidjelli *et al.*[396] found that plasticizer evaporation precedes dehydrochlorination. Their data, similar to that reported by us,[49,50] show that the increase in DOP fraction in formulation causes a proportional increase in thermal stability (compare Figures 4.72 and 4.77). It should be noted that data presented by Marcilla and Beltran[400] and by Djidjelli[396] point in different directions. It is not possible to reconcile results due to experimental differences (Marcilla and Beltran used only one concentration of plasticizer, 65 phr, which was outside the range of concentrations used by Djidjelli *et al.*[396]) and the nature of the method used (thermogravimetry measures mass loss but does not differentiate between plasticizer loss and HCl loss).

Figure 4.78 shows that yellowness index increases (stability of PVC decreases) with DOP concentration. Gonzales-Ortiz *et al.*[92] show a series of chips representing degradation progress of formulations containing 35, 45, and 55 phr DOP and these chips indicate that the color stability of PVC increases with DOP concentration increasing. Jimenez *et al.*[160] show that activation energy of plasticizer evaporation is lower than activation energy

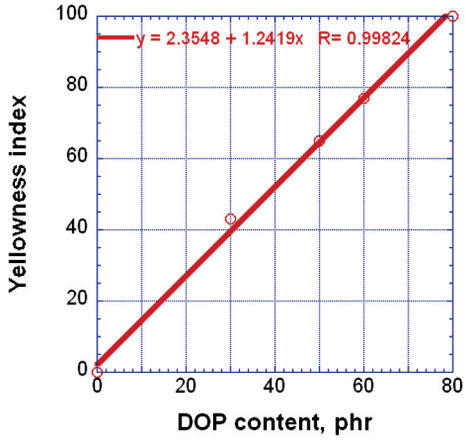


Figure 4.78. Yellowness index of PVC formulations heated in oven for 40 min. at 180°C vs. DOP content. [Data from Gokcel, H. I; Balkose, D., *Adv. Polym. Technol.,* **17**, 1, 63-71, 1998.]

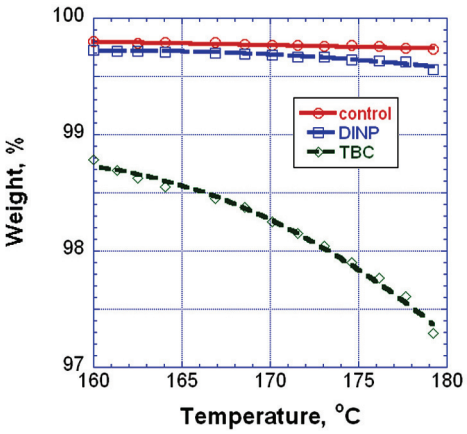


Figure 4.79. Weight vs. temperature for PVC samples containing 40 phr plasticizer studied by thermogravimetry. control - PVC without plasticizer, DINP - diisononyl phthalate, TBC - tributyl citrate. [Data from Gil, N.; Saska, M.; Negulescu, I., *J. Appl. Polym. Sci.*, **102**, 2, 1366-1373, 2006.]

of dehydrochlorination (111 and 145 kJ mol^{-1}, respectively); therefore plasticizer evaporation is more likely to occur.

Figure 4.79 shows that tributyl citrate (and other citrates not shown here) destabilize PVC to a much greater extent than diisononyl phthalate.

In summary of the current literature, it is pertinent that the studies on the effect of plasticizers on thermal degradation of PVC available in open literature address only narrow aspects and therefore do not allow us to draw any fundamental conclusions or evaluate previous fundamental studies. The other problem with the most current studies is that they come from thermogravimetric analysis which does not permit separation of mass loss due to plasticizer evaporation, plasticizer degradation, and dehydrochlorination. Since these three are competing processes occurring simultaneously, it is not possible to understand mechanisms of degradation and its kinetics. It should be noted that this subject is best understood by knowing rates of color change and rates of dehydrochlorination and these are not provided by the current studies.

4.5.12 PROCESS AIDS

Acrylic process aids promote fusion, increase melt strength, increase melt elasticity, and for some particular grades reduce sticking to the metal parts.[314] They are added in small quantities (0.3 to 1.5 phr). Ethylene copolymer resins were studied for application as process aids.[401] These are used at larger concentrations (more like plasticizers). No data can be found on the effect of these additives on thermal stability of PVC.

4.5.13 SOLVENTS

Table 4.6 shows the effect of selected solvents on PVC thermal stability number A.[49,50] Here thermal stability of films (PVC 100 phr, DOP 60 phr, and alcohol 2 phr) was measured using kinetic measurements of HCl evolution and expressed as thermostability number A.[392,393] It is evident that alcohols of higher molecular weight (above six carbon atoms) have very little influence on PVC thermal degradation rate. Only more volatile xylene and isobutanol increase degradation with a rate comparable to the weakest acids.

Table 4.6. Thermal stability of PVC compositions containing various alcohols. [Data from Wypych, J., **Selected properties of PVC plastisols**, *Wroclaw Technical University Press*, 1977.]

Alcohol/rest	Thermostability number A,%
Xylene	50.8
Isobutanol	50.1
Octanol	55.9
2-ethylhexanol	56.4
C7-C9 alcohols	56.7
C9-C11 alcohols	57.1
Decanol	57.1
Isononanol	57.4
Control	60.7

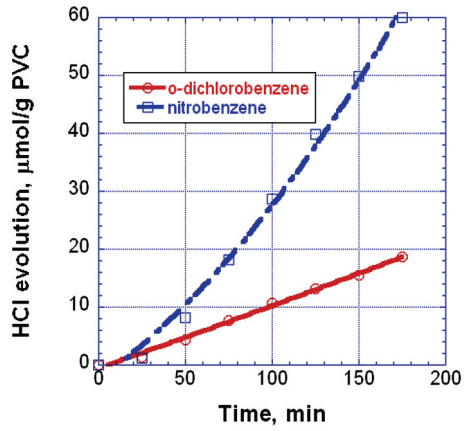


Figure 4.80. HCl evolution from PVC in different solvents vs. degradation time. [Data from Zuoyun, H.; Xinzhou, H, Gang, S., *Polym. Deg. Stab.*, **24**, 127-135, 1989.]

Various principles may be involved in relation to solvent effect on PVC thermal degradation.[4,132,202,402-404] Solvents are known to influence the *cis-trans* isomerization of conjugated double bond sequences.[202] They also create polarons by interacting with conjugated double bonds. These two influences affect dehydrochlorination rate. Solvents influence stereospecific substitution reactions which may affect thermal stability of PVC.[403]

The chemical nature of the solvent, its basicity, specific and nonspecific solvation, concentration of PVC in solution, segmental mobility of macromolecules, thermodynamic properties of the solvent, and the formation of associates and aggregates all affect PVC dehydrochlorination.[404] PVC degradation in solution is affected by a change of the kinetic parameters due to the nucleophilic activation of the PVC dehydrochlorination reaction.[404] There is a linear dependence between the thermal dehydrochlorination rate and a solvent‘s basicity.

Increase in solvent polarity accelerates the PVC thermal dehydrochlorination. Figure 4.80 shows that more polar solvent (nitrobenzene, polarity 4.22) increases degradation rate of PVC as compared with less polar solvent (o-dichlorobenzene, polarity 2.27).

Activation enthalpies and entropies of dehydrochlorination of chloroakenes depend on solvent (non-polar solvents have little influence, polar solvents change mechanism of dehydrochlorination).[4]

Thermal decomposition of PVC was carried out in decalin or tetralin at 300-460ºC for 0-90 min under 4.0 MPa of initial nitrogen pressure.[405] Dechlorination of PVC was almost complete in 30 min at 300ºC.[405]

4.5.14 STABILIZERS

The discussion of influence of stabilizers on thermal degradation of PVC is omitted here because it is fully discussed in Chapter 11.

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5

Principles of UV Degradation

Comparison of chemical changes in molecules excited on the electronic level with molecules whose excitement is thermally induced reveals a significant difference between the mechanisms of these two reactions. Furthermore, they usually lead to entirely different products. In thermal reactions, molecules in their ground state can be elevated to the higher vibrational levels of the electronic ground state by collisions with other molecules or walls, and thermal energy is a factor controlling the frequency and probability of such collisions. Chemical change occurs when some atoms in a particular segment accumulate sufficient energy for bond dissociation. Photochemical reactions, by contrast, involve molecules in electronically excited states. Here the excitation process is more specific of particular chemical moiety as it depends on the quantified energy level needed to achieve molecular excitation. The energy level supplied in the photolytic process depends on the possibility of excitation rather than on its probability and frequency. The following discussion points out to the differences in treatment of photolytic reactions and the thermal degradation processes in order to avoid an unjustified comparison of changes. Thermal degradation is more chaotic, depending on the probability of the energy level, and photodegradation is strictly controlled by the quantum structure of the material undergoing eventual conversion.

Similar to the thermal degradation process, in photolytic degradation, chemical change may occur only when the molecule attains an energy level sufficient to break the weakest bond in the molecule. But it has also been known since the nineteenth century that only the light absorbed by a molecule can possibly be effective in inducing a chemical change. This last observation, known as Grotthus and Draper's law, enforces essential limitations for the occurrence of the photolytic process. In the thermal degradation, when the material temperature is low, there is still a statistical probability that some molecules will have a higher energy than others, which is sufficient to cause a chemical reaction. That is why thermally induced reactions may proceed under a broad range of conditions, and when the energy supply increases, the probability of collisions and the number of molecules or bonds which qualify to undergo chemical change also increase. Photolysis is different, since, first of all, energy has to be absorbed, which is not always the case. Secondly, the energy which was absorbed has to be high enough to “drive away” an electron from its former position. Let us concentrate, for a moment, on these two phenomena.

Fortunately, due to well-developed spectroscopic methods, there is a sufficient amount of information on how absorption of radiation by particular molecules occurs. The degree to which light is absorbed by matter is described by the Lambert-Beer's law, according to which the relative decrease in the incoming beam intensity is proportional to the number of absorbing molecules encountered on its way. We can see that the intensity

of the incoming beam depends (Planck's equation) on the number of photons and their frequency. The number of photons removed from the beam, in turn, depends on the probability of their absorption, and this is a function of the number of absorbing atoms in a unitary volume, sample thickness and, again, the probability that the photon in question will be intercepted by a given atom. It is evident that the model of absorption adapted by Lambert-Beer's law consists of spheres of a particular cross-sectional area embedded in a transparent matrix of a known area and thickness. The probability of photon interception needs more explanation, as it determines the fate of the energy which is absorbed and, moreover, it should explain why one photon is absorbed whereas another is not. First of all, it is important to see that we have to use both of the once-conflicting theories, i.e., particulate and electromagnetic theory. The first has been employed since Planck's equation was adopted, but if it were the only theory applied, how would we reconcile it with the fact that some photons are not absorbed? In quantum physics, both theories do not exclude each other, and the dualistic character of radiation is commonly accepted. In Bohr's model of the atom, the electron of higher energy (excited state of a molecule) is shifted to the orbit of higher energy. The electron energy difference can, therefore, be gained from radiation or released when an electron returns to its former orbit. This type of explanation is still quite common in photochemistry, regardless of the fact that Bohr's model now has only historical value.

Taking into consideration that a light beam is composed of electric and magnetic fields, it is easy to understand why some photons can be absorbed while others cannot. Since electrons and nuclei are charged, it is not surprising that they interact with light. Each photon carries an amount of electromagnetic energy which can be calculated from its frequency. When the radiation arrives at the material, the electrons, which are otherwise in their normal state, are affected by the oscillating electric fields of electromagnetic waves. If the frequency of the light wave and molecular system do not match, the interaction is non-resonant; if they do match, the interaction is resonant. In the first case, the excess energy received by a molecule or atom is usually quite small and it is disposed with great efficiency by re-radiation. If the direction of re-radiation is different than that of the incident beam, the interaction is called light-scattering. Resonant interactions are much stronger than non-resonant ones. The characteristic frequency of absorption is actually a band of frequencies of a certain width. During the act of radiation or absorption of light by matter, the electromagnetic waves constitute fields that are uniform in space but oscillating in time. These fields exert torques upon the oscillatory dipole moments of atoms and molecules. The energy transfer from an electromagnetic field to matter depends on the magnitudes of the corresponding fields and dipoles, the difference in their phases, and the departures of their frequencies from their natural quantum frequency.

The characteristic frequency of absorption can be measured by ultraviolet spectroscopy or estimated according to Franck-Condon's rule for molecular orbitals of the chemical substance under consideration. The details of this treatment may be found in a monograph devoted to material weathering.[1] Below we only include a rudimentary analysis of some aspects of photophysics and photochemistry.

5.1 REASONS FOR POLYMER INSTABILITY

5.1.1 RADIATIVE ENERGY

Visible light, infrared radiation, UV radiation, and γ-rays are each a distinct form of electromagnetic radiation. Each propagate in space as waves of electronic and magnetic fields. Electromagnetic waves can be reflected or refracted at a constant speed:

$$c = \nu \times \lambda \cong 3 \times 10^{8}\ ms^{-1} \qquad [5.1]$$

where:

c	radiation velocity (in vacuum),
ν	radiation frequency,
λ	radiation wavelength.

The fundamental theory of electromagnetic radiation developed by Maxwell is used today to explain some properties of radiation such as light spectrum and its diffraction, polarization, interference, etc. But some properties of radiation cannot be explained by Maxwell's theory. A corpuscular description of electromagnetic radiation, applied by Planck to quantum theory, is used as a mathematical interpretation of the various properties of radiation. According to quantum theory, electromagnetic waves carry discrete amounts of energy, the magnitude of which depends on their frequency, as stated by Planck's Law:

$$E = h \times \nu \qquad [5.2]$$

where:

E	energy of radiation
ν	frequency of radiation
h	Planck's constant.

Eq [5.2] can be used for calculating the energy of radiation of known wavelength. The excitation energy per mole can be obtained by multiplying molecular excitation energy by Avogadro's number:

$$E = Nh\nu = \frac{Nnhc}{\lambda} = \frac{119627}{\lambda}\left[\frac{kJ}{mol}\right] \qquad [5.3]$$

where:

E	energy of radiation of a given wavelength,
N	Avogadro's number = 6.022×10^{23} in mol^{-1}
h	Planck's constant = 6.63×10^{-34} in J s
ν	frequency of radiation
c	velocity of light = 2.998×10^{8} in m s^{-1}
λ	wavelength of radiation in nm.

Table 5.1 gives the energy of radiation for some common energy sources

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Table 5.1. Energy of various types of radiation

Type	Wavelength, nm	Energy, kJ/mol
Far UV	100	1196
Vacuum UV	200	598
Mercury lamp	254	471
Solar cut-off	295	406
Mid-range UV	350	341
End of UV range	390	306
Blue/green light	500	239
Red light	700	171
Near infrared	1000	120
Infrared	5000	24
Hard X-rays, soft γ-rays	0.05	2.4×10^6
Hard γ-rays	0.005	2.4×10^7
Laser	matching	as calculated from eq [5.3]

- the shorter the wavelength, the larger the energy of radiation
- an unfiltered mercury lamp has radiation of higher energy than sunlight
- visible light and infrared radiation both carry energy which can be utilized during photochemical processes (see below)
- x-rays and γ-rays have much higher energy than sunlight. Thus, the results of exposure are not comparable.

Table 5.2 shows the strength of selected bonds.

Table 5.2. Bond strength in polyatomic molecules

Bond	Strength, kJ mol^{-1}	Does sunlight have energy to break the bond?
C–H	420-560	no
C–C	300-720	depends on substituents
C–Cl	320-460	depends on substituents
C–N	120-300	yes
C–O	~1000	no
C=O	500-700	no
H–O	370-500	in most cases no
O–O	150-210	yes
S–O	>550	no

PRINCIPLE OF DEGRADATION

The amount of energy absorbed by a molecule must exceed the bond energy to cause degradation

This principle of degradation carries two important messages:

- energy must be absorbed by a molecule for it to make any changes in molecular structure,
- a change in the energy of radiation source will affect degradation.

The radiation frequency is determined by the conditions under which it was formed. A hypothetical black body was postulated by Planck and used in the development of the law which bears his name. The black body, it is postulated, can absorb and emit radiation of any wavelength. When the temperature of the radiation source increases, its emission spectrum is shifted to the left, meaning that it emits more UV and visible light.

5.1.2 RADIATION INTENSITY

Table 5.3. Intensity of radiation

Quantity	Unit
Radiant energy	J
Radiant energy density	J m^{-3}
Radiant flux	W
Irradiance	W m^{-2}

The energy of laser radiation is the same as the energy of visible light or UV (depending on wavelength). But the fact that laser radiation is substantially more intense (focused or concentrated) is central to the following discussion.

Table 5.3 shows some units of radiation. Laser emits radiation from 1 mW (lasers frequently used in optical experiments) to 10 W (moderately powerful argon laser) and beyond. This power is emitted onto a very small surface area (laser light has high coherence, monochromacity, and a small beam width) usually in the range from 10 μm^2 to 1 mm^2. Irradiance is calculated to be in the range of 10^7-10^8 W m^{-2} (in fact the illuminated surface area is limited by and equal to the wavelength of radiation, and power can be as large as 100 W, giving an irradiance of 10^{13} W m^{-2}). If we compare these values with the mean intensity of sunlight on the Earth's surface (in the range of 10^3 W m^{-2}), it is easy to understand the difference between these two sources of radiation and to explain the effects produced (surface etching by laser beam versus minor changes or no changes at all by sunlight).

This illustrates the importance of the conditions under which the experiment is run and reported. It is useful to pursue the laser example. Laser light delivers 10^{12} to 10^{17} photons/cm^3. At this intensity, several photons will react with a single atom, causing high levels of excitation. Laser light also induces very strong electric fields which can be as much as 100 gigavolts per meter. This inevitably causes changes in orientation, dipole formation, ionization, etc.

The use of pulsed lasers, with their highly ordered (polarized) beams, can selectively excite a single isomer (in the mixture) which has the proper configuration for energy absorption. This is why irradiation by chaotic radiation (e.g., sunrays) will produce totally different results than radiations of high intensities (e.g., lasers). (See differences in mate-

rial reaction to various types of radiation by comparing results of irradiation by sunlight discussed in this chapter and by results of irradiation by other forms of radiation discussed in Chapters 6 and 7).

5.1.3 RADIATION INCIDENCE

Two processes, reflection and scattering, determine the amount of energy crossing a surface of a specimen exposed to radiation. The geometrical relationship between incident, transmitted, and reflected beams is given by Snell's law:

$$n_1 \sin\theta_1 = n_2 \sin\theta_2 \qquad [5.4]$$

where:

n_1 and n_2	refractive indices
θ_1 and θ_2	the angles illustrated in Figure 5.1.

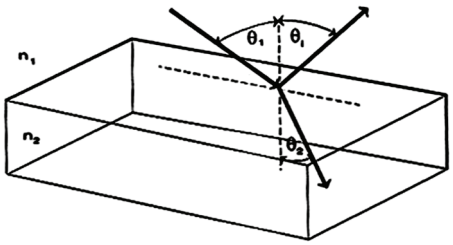


Figure 5.1. Reflection/refraction of radiation.

It should be noted that the angle of incidence and the angle of reflection are equal. Table 5.4 gives refractive indices for some common materials. Using Snell's equation we can calculate that if an incoming beam has an incidence angle of 30°, an angle of transmission, θ_2, is 19.5° (if n_1 equals 1 (for air), and n_2 is assumed equal to 1.5). For any other angle of incidence the transmission angle is smaller than the incidence angle if $n_2 > n_1$. If $n_2 < n_1$, there always exists some critical angle of incidence above which the beam is internally reflected. In practice, specimens are frequently exposed through glass or plastic and/or have a backup of metal, plastic, glass, or other materials. In such cases, refractive indices must be carefully considered when evaluating the effect of the internal reflection of the transparent cover or of the energy retention in the material backing the specimen. Note that the refractive index depends on radiation wavelength (refractive index generally decreases with an increase in wavelength from UV to IR).

Table 5.4. Refractive index, n.

Air	n
Air	1.00
Glass	1.50-1.95
Polymers	1.34-1.65
Water	1.34

It would be helpful to know what proportion of light is reflected from the specimen's surface and what proportion is transmitted into the specimen. Unfortunately, there is no such universal relationship. An understanding of Rayleigh (particle size << wavelength) and Mie scattering (particle size ≈ wavelength) may provide some guidance, although these relationships were developed for particles of very small size (much smaller than the particles in materials dealt with in degradation studies). According to Rayleigh's theory, scattering is proportional to λ^{-4}. This means that shorter wavelengths are preferentially scattered and longer wavelengths are transmitted.

Variations in surface characteristics cause the greatest difficulty in developing a theory to relate refraction and reflection. With a complex surface character, it is very difficult to predict scattering because of the complex geometries involved. Scattering effects diminish the energy which can be transferred to the material.

Comparative specimens must have a similar surface structure. The wavelength of incident radiation must also be the same for any set of samples compared within the range of the experiment.

5.1.4 ABSORPTION OF RADIATION BY MATERIALS

Materials exposed to sunlight receive a very wide spectrum of energy levels. These include the high energy of UV radiation, the lower energy of visible light, and the even lower energy level of infrared radiation. The energy of incoming radiation is quantified such that absorption occurs in one and only one step where all the energy of a single photon is either absorbed or rejected (a quantum of photon energy cannot be divided). This restriction determines which specific wavelength of radiation is absorbed. When UV radiation energy is absorbed by a molecule, the molecule attains an excited state but only when the difference energy between the states before and after absorption equals $h\nu$. The quantity of energy absorbed determines whether a bond can be broken (see Table 5.2). The amount of energy carried by a particular photon (determined by its wavelength) must exactly match the level of energy required by the electronic structure of the molecule for it to absorb this photon and elevate it to its excited state. The difference between the normal and the excited states must be equal $h\nu$. Although this explains the selectivity of this process, it does not fully reflect the complexity of all the processes which occur on exposure.

The energy of radiation may cause different molecular transitions. We have described the so-called electronic transitions in which the position of an electron in the molecule may change from molecular bonding to non-bonding or anti-bonding. These are very drastic changes in molecular structure and they usually require the highest energy levels available in the UV range. But molecules can also undergo transitions in rotational, translational, and vibrational modes which require lesser amounts of energy which are readily available in the visible and infrared radiation. These transitions determine the structure of the molecule in its excited state and it is this structure that determines whether the energy can be safely dissipated or whether the molecule undergoes a permanent change (chemical reaction).

Thus, the selection of conditions of exposure is critical in a weathering study. To underline these important principles of photophysics and photochemistry, two fundamental laws are introduced.

GROTTHUS-DRAPER PRINCIPLE

> Absorption of radiation by any component of the system is the first necessary event leading to photochemical reaction

The Grotthus-Draper Principle, also known as the First Law of Photochemistry, established the essential relationship between cause and effect (see Degradation Principle in Section 5.1.1).

5.1.5 BOND STRUCTURE

From the above discussion we may already draw a conclusion that the labile groups so important in explaining PVC thermal degradation do not have much significance in the description of changes which occur in PVC during its exposure to sun radiation.

Chemical structure of PVC includes three bonds: C–H, C–Cl, and C–C. None of these bonds can be broken by the energy of radiation present in sunrays. For this reason PVC is known to be one of more stable polymers in outdoor use. At the same time, it is known that PVC does degrade on exposure to sun radiation and the particular reasons for this degradation are discussed in the next sections.

5.1.6 THERMAL HISTORY

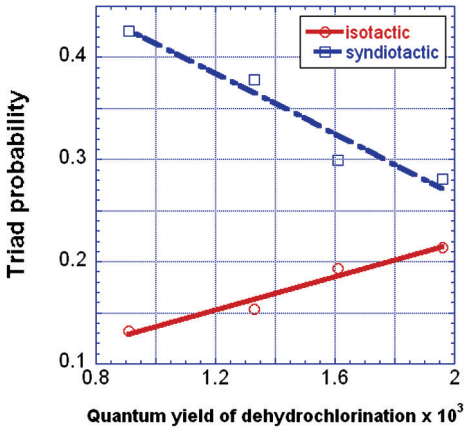


Figure 5.2. The effect of triad concentration on quantum yield of dehydrochlorination. [Data from Castillo, F.; Martinez, G.; Sastre, R.; Millan, J, *Makromol. Chem*., **190**, 477-485, 1989.]

PVC materials are processed before exposure and the severity of the processing conditions determines the extent of material damage. One aspect of this process – dehydrochlorination – was thoroughly discussed in Chapter 4. This process contributes to formation of single and conjugated double bonds of various lengths which depend on conditions (length and severity of processing). Presence of oxygen during processing contributes to further damage because it may oxidize double bonds, create radicals, and then carbonyl groups (see Section 4.1.8).[2]

Morphological changes are less obvious but also important. The energy required for changes in conformation are well within the limits supplied by thermal treatment during processing. Some earlier works show that isotactic triads may be involved in the process of photodehydrochlorination.[3,4] With polymerization temperature decreasing, the concentration of isotactic triads decreases and the concentration of syndiotactic triads increases. The trend for syndiotactic dyads was found to be the same in another study by NMR.[5] Figure 5.2 shows that the hydrogen chloride evolution rate increases with an increase in concentration of isotactic triads.[4] The influence of configuration on absorption of UV radiation is not known. Also, it is not known how configuration may influence excited molecules to make dehydrochlorination a more likely outcome. These findings, similar to the effect of tacticity on thermal degradation, require further studies which may explain the role of conformation in degradative processes.

5.1.7 PHOTOSENSITIZERS

The following sensitizers are known: chromophoric impurities (e.g., hydroperoxides and carbonyl groups), solvents forming hydroperoxides (e.g., tetrahydrofuran), sensitizing

impurities (e.g., benzophenones, hydroquinone, pyrene, 2-acetonaphthanone, 4-hydroxybenzoic acid, 1-naphthol, and 2-phenyl-benzothiazoles), ketoesters, metalorganics (copper-containing compounds, cadmium acetate, ferrocene, iron salts), metal chlorides produced from thermal stabilizers, products of degradation of some antioxidants, some pigments and fillers (containing cadmium, cobalt, zinc, manganese, and lead), metal oxides (of titanium, zinc, and aluminum), and hydrogen chloride (autocatalytic product of PVC degradation).[1,6-8] Impurities catalyze photodegradative processes or absorb UV radiation forming radicals which initiate radical chain reactions.

5.1.8 WAVELENGTH SENSITIVITY

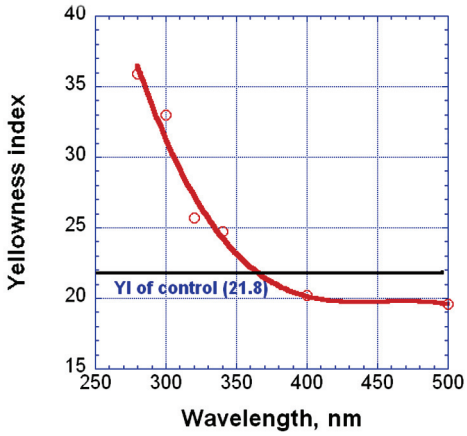


Figure 5.3. Yellowness index of PVC samples exposed to different radiation wavelength. [Data from Andrady, A. L.; Fueki, K.; Torikai, A., *J. Appl. Polym. Sci*., **39**, 763-766, 1990.]

Figure 5.3 characterizes the spectral sensitivity of PVC. The data presented are very reliable because a high precision Okazaki Large Spectrograph was used to irradiate samples with monochromatic light. The original sample had a yellowness index of 21.8 before its exposure to radiation. It is pertinent from the graph that wavelengths of 280, 300, 320 and 340 nm were causing samples to change color to yellow but wavelengths of 400 and 500 nm had photobleaching action. This shows some limits of estimation changes according to color difference. If sun radiation is used, samples undergo yellowing and photobleaching at the same time; therefore, readings of resultant color include two opposing processes. The results also show one of the reasons for the excellent color performance of PVC during environmental exposures.[9,10] Similar results were obtained[11] using Weather-Ometer exposures and cut-off filter technique. The maximum spectral sensitivity was determined to be 300 nm. Radiation above 340 nm has a very small influence on PVC yellowing.

5.1.9 THERMAL VARIABILITY

Fischer *et al.*[12] conducted exposures of PVC specimens in Florida and Arizona in open and backed racks and black boxes. Temperature of samples at various positions in the racks was controlled by thermocouples. Color shift and gloss retention of specimens were measured. In the presented results, the temperature varied depending on the position of specimen in the rack. The rack specimens on edges were always the coolest. Color and gloss changes followed temperature distribution. The smallest changes occurred in samples placed at the edges of the racks where temperatures were the lowest. This experiment demonstrates the importance of temperature on PVC degradation during exposure and the effect of temperature of exposure on the mechanism of photolytic degradation of PVC.

5.1.10 POLLUTANTS

The effect on PVC samples of the most common air pollutants, including ozone, nitrogen oxides (NO and NO_2), and hydrocarbons has been studied.[13,14] The effect of pollutants was studied by exposure in three sites having different concentrations of degradants but very similar weather conditions. Ozone was found to be the most degrading out of the pollutants studied followed by hydrocarbons. Nitrogen oxides did not have a strong influence on properties of rigid PVC.

Chemical analysis showed increased photooxidation (carbonyl, hydroperoxide, and polyene formation). This was accompanied by chain scission which resulted in rapid loss of mechanical properties.[13]

The effect of other pollutants, such as hydrogen species, carbon oxides, sulfur-containing components, chlorine-containing components, and particulate materials has not been studied.

5.1.11 HUMIDITY

Four PVC formulations were studied under different conditions of exposure (including and excluding water jets and humidity).[15] Water jets removed degraded material from the surface of exposed samples causing exposure of "new" surfaces to weathering.[15] It was suggested that the presence of water jets and humidity is required in studies which are to simulate natural conditions.[15]

Studies of the effect of water on photodegradation of PVC samples were also conducted in a closed loop photoreactor which permits measurement of CO_2 evolved.[16] Relative humidity was controlled by salt solutions and bypass control.[16] At very low humidity, the CO_2 evolution rate from PVC was low, but increased to a peak at around 35% relative humidity.[16] At higher humidity levels, the CO_2 evolution rate decreased. The CO_2 emission was catalyzed by HCl.[16] It was found that addition of hydrotalcite reduced CO_2 evolution.[16]

5.1.12 LABORATORY DEGRADATION CONDITIONS

PVC may be used as a classic example to show principles of selection of laboratory equipment for laboratory studies of its photodegradation. Section 5.1.8 shows that PVC changes color to yellow when exposed to radiation in the range of 280 to 340 nm but the yellow color reverses when samples are exposed to visible radiation of 400 and 500 nm. If an instrument, such as a fluorescent lamp device, is selected, it will induce color changes without showing the effect of photobleaching because its spectrum ends at 360 nm.

The experiment discussed in Section 5.1.9 shows that the temperature variability (even as small as 3-8^{o}C) results in a gloss difference of up to 30 units. Selection of an instrument which has an uneven temperature distribution results in a large error of determination. This will concern all instruments which rely on convection in the distribution of air in the test chambers.

5.2 MECHANISMS OF DEGRADATION

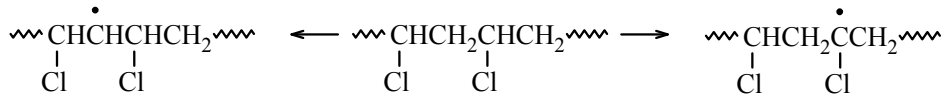
5.2.1 RADICAL MECHANISM

A group of French scientists presented research data and laid down a foundation for our present understanding of the mechanism of PVC photodegradation. There were two groups involved, proposing two slightly different mechanisms which will be discussed below for clarity under the names of photooxidation mechanism[17-24] and mechanistic scheme.[25-29]

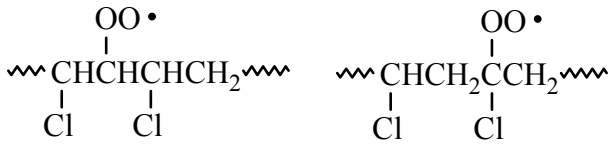
5.2.1.1 Photooxidation mechanism

Gardette *et al*.[17-24] used FTIR of original and derivatized products of photodegradation for identification of photoproducts. The following elements of the photooxidation mechanism were outlined:[17]

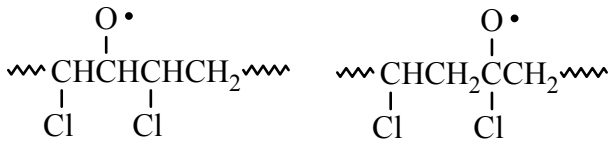
- hydrogen abstraction leads to one of two possible radicals:



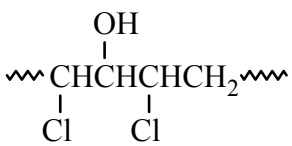
- the above radicals react with molecular oxygen to form a peroxyradical (the radical on the right hand side is more probable):



- hydroperoxides are formed and accumulate at some low stationary concentration,
- O–O bond is then homolyzed (either thermolytic or photolytic reaction) and macroradicals are obtained:



- abstraction of hydrogen from polymer backbone by the radical on the left hand side leads to an alcohol:



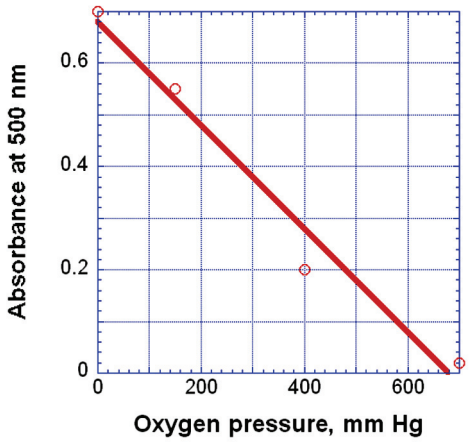


Figure 5.4. The effect of oxygen pressure on absorbance at 500 nm. [Data from Gardette, J. L.; Gaumet, S.; Philippart, J. L., *J. Appl. Polym. Sci.*, **48**, 11, 1885-95, 1993.]

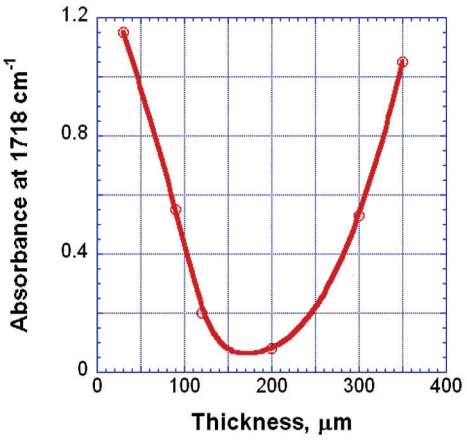
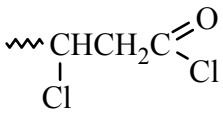


Figure 5.5. The effect of distance from the surface on absorbance at 1718 cm^{-1}. [Data from Gardette, J. L.; Gaumet, S.; Philippart, J. L., *J. Appl. Polym. Sci.*, **48**, 11, 1885-95, 1993.]

- β-scission of alkoxy radical on the right hand side leads to acid chloride:



- hydrolysis of acid chloride leads to carboxylic acid,
- ketones are formed by cage reaction between alkoxy radical on the left hand side and a hydroxy radical,
- some other absorptions were detected in the course of studies and these may be due to the presence of β-chloroanhydride and some α,β-conjugated ketone groups. These groups could not be properly identified.[17]

The above initial results were further investigated[18-24] to confirm the proposed mechanism and understand some of its features. Figure 5.4 shows the effect of oxygen pressure, on PVC discoloration measured at 500 nm. The higher the oxygen pressure the lower the discoloration. Figure 5.5 shows the reason. Carboxyl groups absorb IR at 1718 cm^{-1}. From the chemical reactions given above, we can see that the carboxyl group is formed from oxidation of radicals formed by hydrogen abstraction. Hydrogen abstraction requires UV radiation and oxidation requires oxygen. Oxygen concentration in the sample increases with its pressure and it is substantially higher on both surfaces of the sample; that is why there is less formation of polyenes but oxygenated forms are produced. If the sample is starved of oxygen either because it is not present (vacuum) or diffusion is too slow (sample layer closer to core), the sample discolors by formation of polyenes.[18]

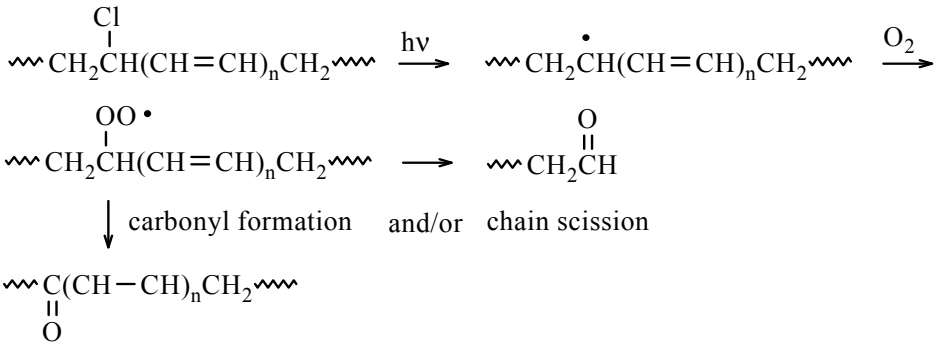
In the beginning of exposure, the oxidation on both surfaces is almost symmetrical but becomes unsymmetrical when exposure time increases. It is because exposure leads to

accumulation of absorbing species which absorb part of the radiation before it reaches the back of the sample (screening effect). Also, sample thickness affects photochemical processes. Approximately the first 150 μm from the sample surface is being oxidized. Thick samples have a thicker core which is not affected (or less affected) by exposure. Also, temperature of exposure plays a role. If temperature decreases from 60 to 35°C, the rate of photooxidation decreases (activation energy of PVC photooxidation is believed to be in the range 50-63 kJ mol^{-1}).[18]

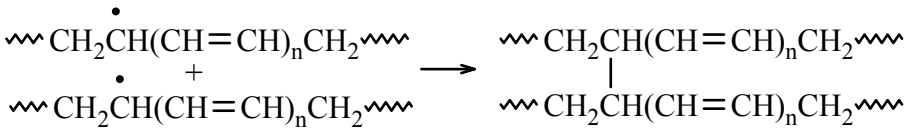
The above findings are of fundamental importance applicable to any polymer affected by photooxidation. They show that the result of photooxidation depends on two factors: the depth of penetration of radiation and the rate of oxygen diffusion. Depending on the interplay of these two factors, changes either occur on the surface or they affect the structure of material beneath the surface.

Further studies[19] concentrated on the formation of polyenes. It was found that in the presence of titanium dioxide, PVC undergoes a latent discoloration that is revealed only during storage of the aged material in the dark. This effect is reversible, and photobleaching occurs when polymer is exposed to radiation. The behavior is attributed to the formation of polyenic sequences with a short conjugation length absorbing below 400 nm. The pigment protects these polyenes from photooxidation and polyenes accumulate in the degraded polymer. In the absence of light, these polyenes can be thermally isomerized to form a species absorbing at longer wavelength (above 400 nm), and this causes yellowing. When this polymer is exposed to radiation it isomerizes back to isomers absorbing below 400 nm, which photobleaches the sample.[19] These changes do not affect mechanical properties. More extensive treatment of color changes is included below in the section devoted to pigments.

The above description of the radical mechanism does not describe details of chain scission and crosslinking. Torikai and Hasagawa[30] have done work on the influence of UV radiation of different wavelengths on chain scission and crosslinking. They propose the following mechanism to explain crosslinking:



The polyenyl radical may also recombine to form a THF insoluble fraction produced by crosslinking:



The above mechanism explains the main features of the photodegradation process by UV radiation. The effects of codegradants and other influences are discussed in next sections.

5.2.1.2 Mechanistic scheme

The mechanistic scheme proposed by Anton-Prinet *et al.*[25-29] differs in some important aspects from the photooxidation mechanism discussed above. The photochemical changes are also attributed to the radical processes but the initiation mechanism differs. Unlike in Gardette's mechanism where initiation is caused by (unspecified) hydrogen abstraction, in this scheme, hydroperoxides (the source of which is also not specified – presumably coming from thermal degradation) are the major initiation species.

Polyenes are not considered to be initiators of a photochain because short polyenes (up to 2 conjugated double bonds) cannot absorb sun radiation (they absorb below 300 nm). It is not explained in the literature how these short polyenes grow. It is suspected that they grow due to HCl catalysis and temperature controlled processes. Polyenes having at least 3 conjugated double bonds grow on irradiation.[27]

Figure 5.6 shows that there is a difference between compositional changes on the surface and inside the sample. At the surface the probability of chain scission is very high because oxygen is in almost unlimited supply. Further into the depth of the sample, the oxygen supply decreases because it is diffusion-controlled, which is a slow process, and crosslinking processes begin to dominate. At the depth of about 200 μm, chain scission ceases to occur because oxygen is completely used up before it reaches such depth.

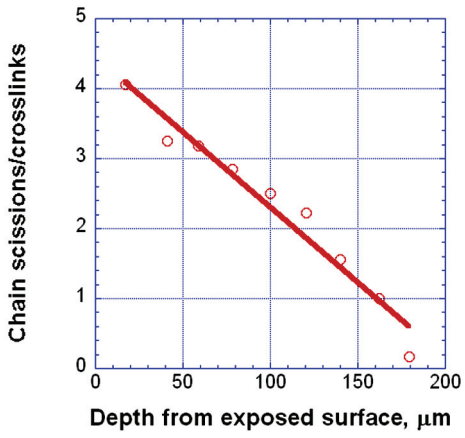


Figure 5.6. The ratio of chain scissions to crosslinks vs. the depth from the exposed surface. [Adapted, by permission from Anton-Prinet, C.; Dubois, J.; Mur, G.; Gay, M.; Audouin, L.; Verdu, J., *Polym. Deg. Stab.*, **60**, 275-281, 1998.]

According to Anton-Prinet *et al.*[25] a PVC sample after exposure is built of three layers. The surface layer, about 50 μm thick, is an oxidized layer in which oxidation reactions prevail. The second layer, about 200-300 μm thick, is a colored layer in which polyenes are propagating which results in color change. Beyond these surface layers is a undegraded core.[25] These photochemical reactions occur as deep as

possible before they become limited by the physical properties of the sample (the presence of oxygen for chain scission, UV radiation for polyene propagation and crosslinking).

The mechanistic scheme assumes that crosslinking reactions may occur by recombination of oxygen-containing radicals or a polyenyl radical (as in the photooxidation mechanism):

$$P^{\bullet} + PO_2^{\bullet} \longrightarrow POOP$$
$$PO_2^{\bullet} + PO_2^{\bullet} \longrightarrow POOP + O_2$$
$$P^{\bullet} + P^{\bullet} \longrightarrow PP$$

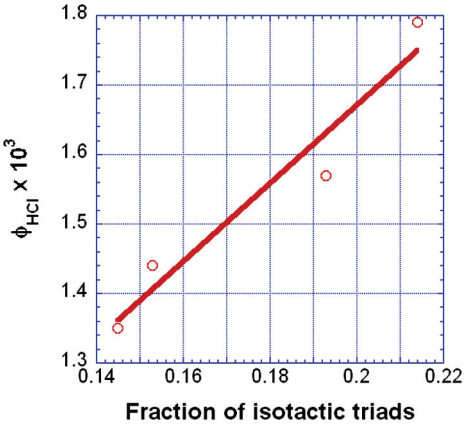


Figure 5.7. Quantum yield of dehydrochlorination, ϕ_{HCl}, vs. fraction of isotactic triads. [Adapted, by permission from Castillo, F.; Martinez, G.; Sastre, R.; Millan, J.; Bellenger, V.; Gupta, B. D.; Verdu, J., *Polym. Deg. Stab.*, **27**, 1-11, 1990.]

The first two reactions, although possible, produce highly reactive peroxides, which reinitiate chains of reaction.[25] As exposure time increases and degradation of the surface layer progresses, the superficial layer becomes embrittled by oxidative chain scissions and cracks under external loading, differential expansion, or density gradients induced by photoaging. The surface layer is then removed by natural forces (wind, washing, etc.), and polyenes underneath lack their "protective layer" and undergo photobleaching, which moves the boundary zone towards the sample core.

We may see from the above description that both mechanisms discussed so far are complementary to each other. They are both weak in explaining the initiation of chain reaction and propagation of polyenes.

5.2.1.3 Conformational mechanism

Castillo *et al.*[7,30] presented results of their studies in which they considered the effect of structure on dehydrochlorination of PVC samples during exposure to UV. Two types of samples were studied:

- samples of polymers obtained at temperatures ranging from -30 to 90°C. In these samples, increase in polymerization temperature contributes to increase of a fraction of isotactic triads, and, as Figure 5.7 shows, the quantum yield of dehydrochlorination. These studies were conducted under oxygen.
- samples of a polymer subjected to fractionation in acetone. Three samples were studied: polymer as received, acetone soluble, and insoluble fractions. Studies were conducted under nitrogen.

It was discovered that in both cases, the quantum yield of dehydrochlorination depended on the concentration of isotactic triads and it had the same relationship under oxygen and nitrogen. This has prompted the authors of studies to analyze the reasons for

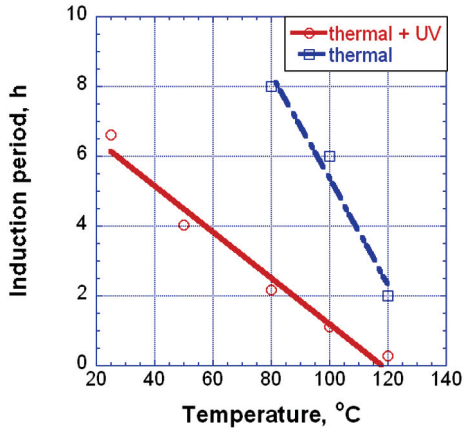


Figure 5.8. Induction period vs. temperature of thermal degradation for samples degraded only by thermal exposure and by the combined thermal and UV exposure. [Adapted, by permission, from Rabek, J. F.; Ranby, B.; Skowronski, T. A., *Macromolecules*, **18**, 1810-1818, 1985.]

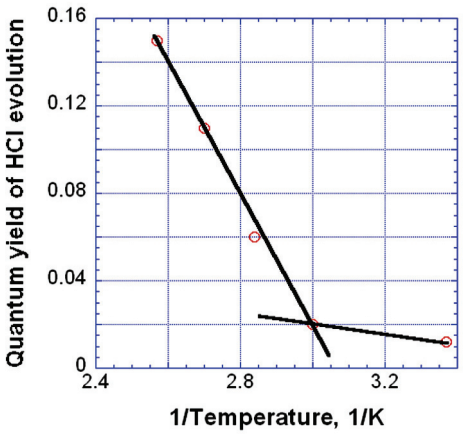


Figure 5.9. Quantum yield of HCl evolution vs. temperature during photothermal dehydrochlorination of PVC. [Adapted, by permission, from Rabek, J. F.; Ranby, B.; Skowronski, T. A., *Macromolecules*, **18**, 1810-1818, 1985.]

such a relationship, which may be essential for the mechanism of PVC dehydrochlorination on exposure to UV radiation.

Following suggestions from Reinisch *et al*.,[31] they proposed that the concerted dehydrochlorination is only possible when the skeleton bond to be transformed into a new double bond is coplanar to the polyenic sequence.

The chlorine atoms located in the isotactic GTTG$^-$ triad conformation have low dissociation energy. Also, the subsequent hydrogen abstraction reactions are more difficult because of shielding of hydrogen atoms at the isotactic triads. The above results may show that these labile chlorines are initiation sites of photodegradation.

5.2.1.4 Electronic-to-vibrational energy transfer

Rabek *et al*.[32] proposed electronic-to-vibrational energy transfer to explain the reasons for rapid dehydrochlorination observed during photothermal decomposition of PVC. Figures 5.8 and 5.9 contain information on the reasons and experimental details.[32] Figure 5.8 shows that simultaneous application of two stresses (UV and thermal energy) substantially shortens induction period (increases the degradation rate). Figure 5.9 shows that there are two rates of photothermal degradation: at lower temperatures (below glass transition temperature of PVC) and the other substantially higher at higher temperatures (above the glass transition temperature).

Below the glass transition temperature of PVC (82^{o}C) chain segments are frozen in fixed positions in a disordered quasi-lattice. When temperature increases, the amplitude of segmental vibrations increases. In the rubbery state the segmental motions are very rapid, but the molecular motion (the motion of the entire molecule) is restricted by chain entanglements. Further increase in temperature causes reduction of the degree of entangle-

ments. But also, diffusion of HCl to the sample surrounding increases and the probability of catalyzed reaction decreases. Such changes cannot simply explain the rapid evolution of HC1 during photothermal dehydrochlorination of PVC.

The proposed electronic-to-vibrational energy transfer mechanism may help us to understand the observed changes. With increasing temperature, the thermal excitation of a given bond increases because vibrational energy of a bond increases. If the energy of excitation is higher than the energy of dissociation of the C–Cl bond, the formation of polymer alkyl and chlorine radicals occurs.[32] If molecules with an increased vibrational energy absorb radiation, the electronic-to-vibrational energy transfer occurs, and a given bond may have enough excess energy to dissociate into free radicals. The effect of the addition of two types of energy: the thermal energy and the radiative energy by the proposed electronic-to-vibrational energy transfer seems to explain the rapid increase of dehydrochlorination when two types of energy are simultaneously applied.[32]

5.2.1.5 Other contributions to the mechanism of photodegradation

Comparison of photoreactions under nitrogen and oxygen shows that carbonyl groups are also formed under nitrogen, although at a slower pace.[33] Photodegradative processes under nitrogen take advantage of hydroperoxides formed during thermal processing and these hydroperoxides are converted to carbonyl groups.[33]

XPS analysis of virgin polymers indicates the presence of carbonyl groups in small quantities. These carbonyl groups are formed during the polymerization process in the polymer backbone and as side groups containing carbonyl chlorides.[34] Although their concentration is small, they are believed to contribute to photo-instability of PVC.[34]

Water is an essential element in degradative processes. There are two reasons:

- water affects photocatalytic activity of titanium dioxide (this subject is discussed in Section 5.5)
- rain and wind contribute to the refreshing of the surface of degrading PVC by removing degraded surface layers, extracting components of formulation, and reduction of concentration of oxidized products,[35]
- rain also deposits pollutants (e.g., sulfuric acid) on the surface dissolved, which react with fillers (e.g., calcium carbonate) and modify the surface properties of PVC articles.[36]

Plasticizer loss is one very essential mode of PVC degradation on exposure to natural and laboratory environments.[37-39] It was established in plasticized PVC that the main loss of its properties is related to the loss of plasticizer.[37] Figure 5.10 shows that the loss of DOP on natural exposure is an almost linear function of time.[37] Plasticizer is partially lost by diffusion but also because of its own degradation (see more on this subject in Section 5.5.7).[38] Figure 5.11 shows that loss of plasticizer increases porosity of material which opens its structure to a more extensive diffusion of oxygen.[37]

The activation energy of PVC discoloration were calculated as 6.1 kJ/mol for Δb^* and 7.4 kJ/mol for ΔE^*.[38] The C=O and C–O groups contributed little to the color change of PVC.[38]

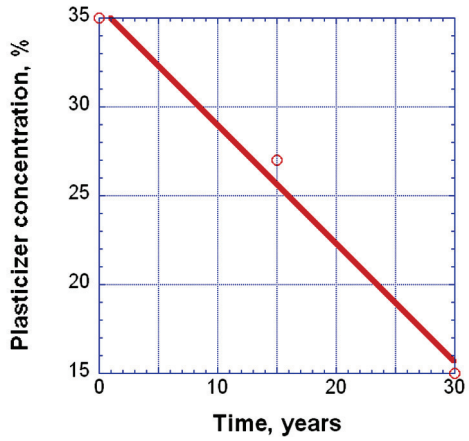


Figure 5.10. DOP loss during natural use of cables. [Data from Gumargalieva, K. Z.; Ivanov, V. B.; Zaikov, G. E.; Moiseev, Ju. V.; Pokholok, T. V., *Polym. Deg. Stab.*, **52**, 1, 73-79, 1996.]

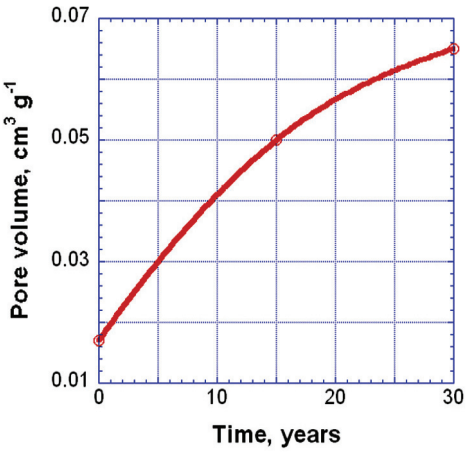


Figure 5.11. Porosity of cables material vs. exposure time. [Data from Gumargalieva, K. Z.; Ivanov, V. B.; Zaikov, G. E.; Moiseev, Ju. V.; Pokholok, T. V., *Polym. Deg. Stab.*, **52**, 1, 73-79, 1996.]

5.3 KINETICS

5.3.1 INITIATION

Several chemical groups are considered as initiation sites. These include: unsaturations,[41,42] carbonyls,[42] hydroperoxides,[25,29,42] impurities,[11] and additives.[11] The common feature of all initiation sites is that they must be able to absorb in the UV range. The following equation was proposed by Anton-Prinet *et al*.[29] to calculate the initiation rate:

$$r_i = \alpha k_I[POOH] + \alpha' k'_I[POOH] = K_i[POOH] \quad [5.5]$$

$$K_i = \alpha\Phi I + \alpha' k'_{Io}\exp(-E_I/RT) \quad [5.6]$$

where:

α	radicals formed from hydroperoxide by absorption of UV radiation,
k_I	constant of reaction of radical formation by UV absorption,
[POOH]	concentration of hydroperoxides,
α'	radical formed by thermolysis,
k'_I	constant of reaction of radical formation by thermolysis of hydroperoxide,
Φ	quantum yield of photolysis,
I	light intensity,
k'_{Io}	constant of Arrhenius equation,
E_I	apparent activation energy,
R	gas constant,
T	absolute temperature.

A steady state of radical chain oxidation is rapidly reached when POOH destruction equilibrates POOH formation.[29]

5.3.2 PROPAGATION

Propagation is not an adequate title. It is used here to relate the description of kinetics to the kinetics of thermal degradation. Unlike in the case of thermal degradation, here we do not have one dominating reaction (dehydrochlorination) which can be monitored to extract information on kinetics of propagation process.

Propagation needs radiative energy and oxygen presence and these are variable, unlike the constant supply of thermal energy in the thermal degradation processes. From the chemical point of view, polyenes formation is in some equilibrium with their oxidation, which again differs from the time-related growth of polyenes in the thermal degradation processes.

Propagation of polyene growth in photothermal processes, according to some studies, results from thermal degradation.[29,31] It is possible that polyenes grow partially because of thermal energy, and this process may be described by the same kinetic equation which is used in thermal degradation studies (eq. [4.11]). At the same time, it should be considered that under outdoor exposure, sample temperature may increase to a maximum 110°C, and at this temperature, thermal dehydrochlorination is too slow to explain polyene formation rate. Figure 5.8 shows that UV radiation increases the rate of dehydrochlorination; therefore, there must be some additional quantity of HCl produced with assistance of UV energy.

Zhuravlev and Ivanov[43] proposed the following equation for estimation of the formation rate of polyenes:

$$w_n = \alpha_n w_0 \frac{k_I}{k_l + (k_I + k_l)\dfrac{k_{l,I}}{k_{eff}}} \qquad [5.7]$$

where:

α_n	polyene length factor,
w_0	initiation rate,
k_I	double bond formation rate,
k_l	rate of formation of stable products from alkyl radical (end of growth for this site),
$k_{l,I}$	rate of formation of stable products from polyene radical (end of growth for this site),
k_{eff}	rate of polyene propagation.

The effect of tacticity on propagation is not clear. According to one source syndiotactic sequences promote polyene growth,[30] and their effect is considered insignificant according to another publication.[44]

Activation energies calculated from the linear relationships of photodehydrochlorination rate vs. temperature show that the degradation process in nitrogen is slower than in air ($E_{a(nitrogen)}$=32.1 kJ mol^{-1} and $E_{a(air)}$=19.6 kJ mol^{-1}).[45] After photodegradation under an oxygen atmosphere, the maximum concentration of polyenes is found at depths of 30-60 μm, with a monotone decrease deeper into the polymer.[46] Under an inert atmosphere, the maximum concentration of polyenes is in a 5-10 μm superficial layer of the sample.[46] The propagation of polyenes deeper into the sample is prevented by formation of chromophore centers (polyenes) which screen radiation. During exposure, light absorption increases. A virgin, homogeneous sample obeys the Beer-Lambert law:[26]

$$I = I_0 \exp(-\varepsilon P x) \quad [5.8]$$

where:

I_0	intensity of incident beam,
ε	molar absorptivity of UV absorbing species,
P	concentration of UV absorbing species,
x	length.

At the beginning of the exposure, oxidation is limited by oxygen diffusion but increased polyene concentration leads to an increased concentration of UV absorbing species and after a certain period of oxidation, the thickness of the oxidized layer becomes controlled by the polyene screening effect. This prevents any further progression of the oxidation front towards the core.

During natural weathering, the photochemical production of polyenes and their subsequent thermooxidation seems to occur simultaneously.[47] Polyenes in materials exposed to UV radiation are shorter than polyenes produced during thermal degradation because of photooxidation of some double bonds. In laboratory studies, some of the processes occurring in outdoor exposure are not properly reproduced because of differences in radiation spectrum, temperature, and omission of light and dark cycles.

Both plasticized and pure PVC powder had the same activation energy of photodegradation at 150 kJ/mol.[48]

5.3.3 TERMINATION

Termination of photochemical reaction may occur because of physical and chemical reasons. Physical reasons were well described in the previous paragraph and they include either lack of oxygen near the excited sites or lack of radiative energy because of the polyene screening effect.

Equation [5.8] outlines the limits of radiative energy penetration. Equation [5.9] outlines kinetic controls of oxygen diffusion:[27]

$$\frac{dC}{dt} = D\frac{d^2C}{Cx^2} - r(C) \quad [5.9]$$

where:

C	oxygen concentration,
t	time,
D	oxygen diffusion coefficient,
x	depth of the layer,
r(C)	rate of oxygen consumption.

Oxygen concentration depends on the oxygen partial pressure in the surrounding atmosphere and temperature which affects the diffusion rate of oxygen (Figure 5.12). The temperature range presented in Figure 5.12 is still below the glass transition temperature for rigid PVC. Rapid increase can be expected at higher temperatures (up to the limit of typical exposure temperatures (up to 110°C)). Figure 5.13 shows that carbonyl formation rate increases with the increase in oxygen partial pressure.[27] Considering that the variable

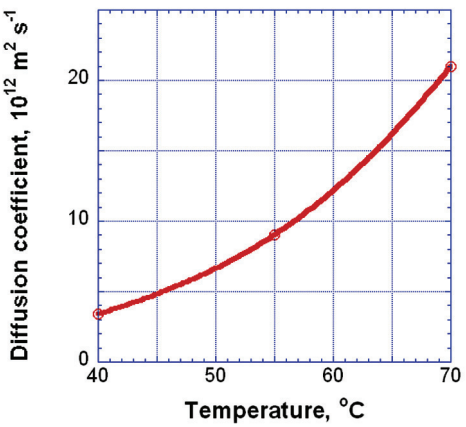


Figure 5.12. The oxygen diffusion coefficient vs. temperature. [Data from Anton-Prinet, C.; Mur, G.; Gay, M.; Audouin, L.; Verdu, J., *Polym. Deg. Stab.*, **61**, 2, 211-216, 1998.]

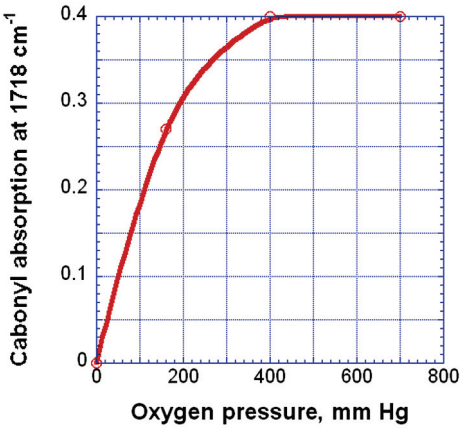


Figure 5.13. Carbonyl formation vs. oxygen pressure. [Adapted, by permission, from Anton-Prinet, C.; Mur, G.; Gay, M.; Audouin, L.; Verdu, J., *Polym. Deg. Stab.*, **61**, 2, 211-216, 1998.]

range is within the concentration of oxygen in air, it can be expected that oxygen starvation affects oxidative processes close to the surface (as experimental results show – see previous section).

Chemical reasons for termination include all processes discussed in Section 4.3.3 since, at least partially, thermal processes are responsible for propagation of polyene growth. In addition, the radical processes of photooxidation (and polyene growth) can only be terminated for a particular site if any radicals recombine.[49] In addition to random occurrences of recombination, the restricted mobility of the free radical fragments in a solid polymer irradiated at temperatures below glass transition temperature (87°C for rigid PVC) favor radical recombination (if PVC is photolyzed in solution, where cage reactions are less likely to occur, the quantum yield of initiating radicals are found to be much larger and dehydrochlorination proceeds 10 times more efficiently).[50]

It is clear from the comparison of thermal and UV degradation that many details of kinetic processes are lacking.

5.4 RESULTS OF UV DEGRADATION

5.4.1 PHOTODISCOLORATION

Photodiscoloration is controlled by the time of exposure (Figure 5.14), oxygen diffusion (and partial pressure) (Figures 5.4 and 5.14), and wavelength of radiation (Figures 5.3 and 5.15).

Figure 5.14 shows that discoloration of PVC samples increases with time of exposure in both vacuum and at lower pressure of oxygen.[18] Figure 5.4 shows that increase of oxygen pressure has a dramatic influence on discoloration because oxygen diffusion is increased and oxidation of double bonds prevails over their formation.

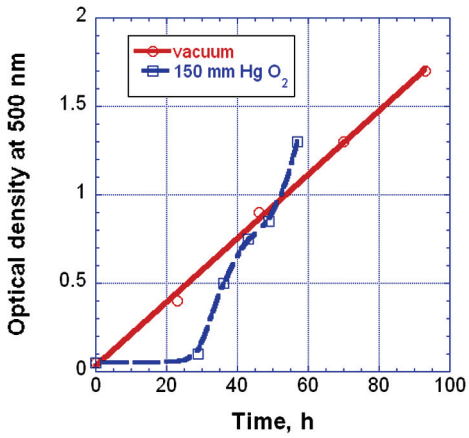


Figure 5.14. Discoloration vs. time of exposure in SEPAP in vacuum and under oxygen with partial pressure of 150 mm Hg. [Data from Gardette, J. L.; Gaumet, S.; Philippart, J. L., *J. Appl. Polym. Sci.*, **48**, 11, 1885-95, 1993.]

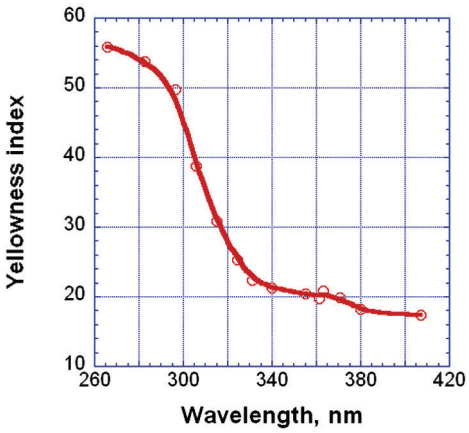


Figure 5.15 Yellowness index vs. cut-off wavelength of filter. [Data from Andrady, A. L.; Searle, N. D., *J. Appl. Polym. Sci.*, **37**, 2789-2802, 1989.]

Two methods of testing the wavelength effect on discoloration were used.[9-11] In one of the methods,[9,10] samples were exposed to the monochromatic light in the Okazaki spectrograph; in the other method, cut-off filters were used. It can be seen that both methods produced similar results. In the case of the Okazaki spectrograph exposure, yellowness index decreased with increasing radiation wavelength until to about 360 nm, discoloration begins to decrease below the discoloration of an unexposed sample, meaning that radiation wavelength above 360 nm caused photobleaching. In Figure 5.15, photobleaching begins to occur below 340 nm.[11] Earlier photobleaching in the case of cut-off filers (Figure 5.15) can be explained by the differences in temperature. In the Okazaki spectrograph, samples were exposed at 25°C and, although temperature of exposure in a Weather-Ometer with cut-off filter is not given, it must have been much higher (at least 65°C), because experiments are typically conducted at higher temperatures and samples were almost covered with filter and exposed on a black background (filter was positioned at the distance of 1/8 inch above the sample). Proximity of filter would limit air flow over the sample and thus increase temperature.

Figure 5.16 shows that exposure to processing temperatures is the reason for formation of carbonyl groups and that carbonyl groups contribute to discoloration (Figure 5.17) by increasing absorption of radiation and increasing the number of the conjugated double bonds.[51]

The above information regards samples which were not stabilized against UV radiation. Section 5.5.6 below contains information which is more characteristic of commercial formulations.

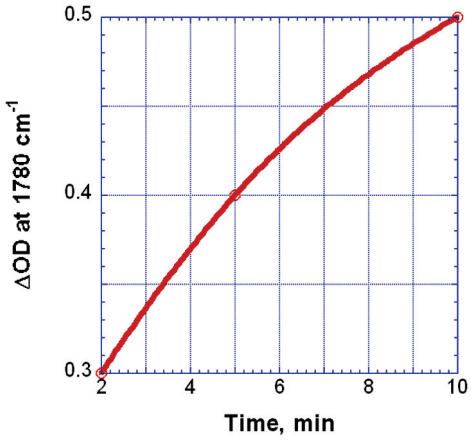


Figure 5.16. Carbonyl group formation vs. processing time. [Data from Gervat, L.; Morel, P., *J. Vinyl Additive Technol.*, **2**, 1, 37-43, 1996.]

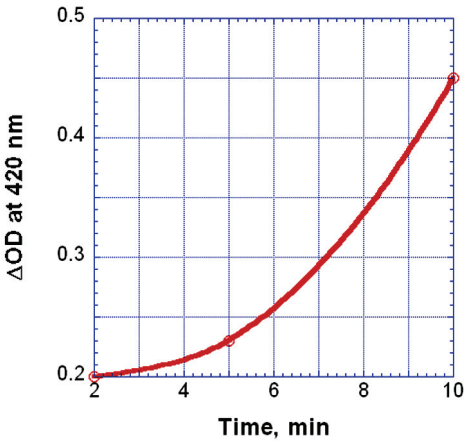


Figure 5.17. Color change vs. processing time. [Data from Gervat, L.; Morel, P., *J. Vinyl Additive Technol.*, **2**, 1, 37-43, 1996.]

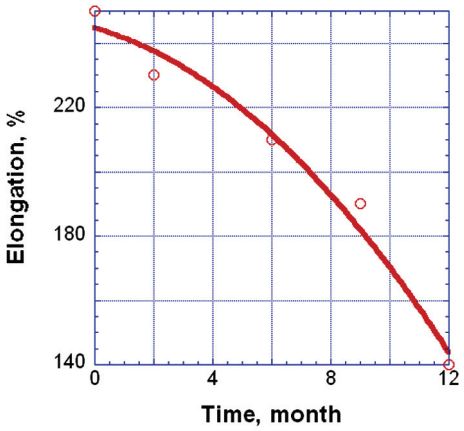


Figure 5.18. Changes of elongation of plasticized PVC during outdoor exposure. [Data from Gerlach, D., *Plastics, Rubber Composites*, **34**, 3, 117-120, 2005.]

5.4.2 MECHANICAL PROPERTIES

Figure 5.18 shows changes in elongation at break during natural exposure. It should be noted that most of these changes are due to loss of plasticizer (DOP and DOA).[48] Figure 5.19 shows that tensile strength is even less affected than elongation (4% drop vs. 10% drop in elongation in the same study).[39] Figure 5.20 shows that temperature during photolytic degradation affects its rate.[25]

Figure 5.21 shows that outdoor exposure in Algeria causes considerable loss of tensile strength of rigid PVC. The exposure site contains high concentrations of ozone (10-100 ppb). When samples were exposed in areas which did not contain these high concentrations of ozone the decrease in tensile strength was considerably less – about 6% vs. 14% in high ozone location).

Window-grade PVC formulation was monitored by Vicker's hardness during natural and artificial exposure.[53] Only small changes were detected because the core is not affected and the surface is continuously changed due to surface erosion process.[53] A similar conclusion can be reached based on microhardness measurements.[54]

Impact strength readings are affected by the presence of a degraded layer on the surface of PVC materials. Figure 5.22 shows results of impact strength measurement of five

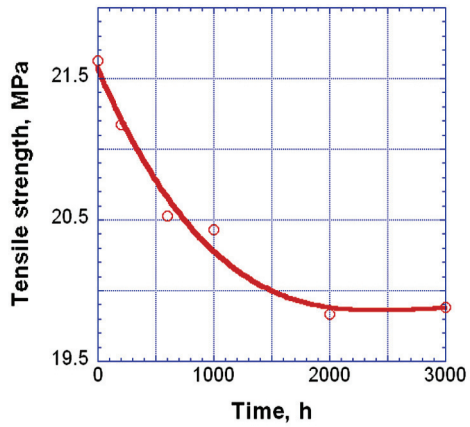


Figure 5.19. Tensile strength vs. time of exposure in WEL-SUN-DC. [Data from Ito, M.; Nagai, K., *Polym. Deg. Stab.*, **92**, 2, 260-270, 2007.]

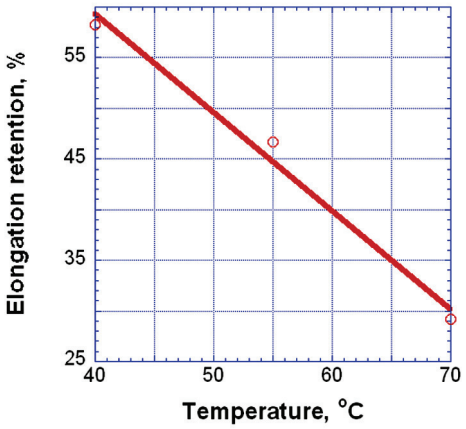


Figure 5.20. Elongation retention after exposure for 600 h to radiation from 300 to 450 nm vs. exposure temperature. [Data from Anton-Prinet, C.; Dubois, J.; Mur, G.; Gay, M.; Audouin, L.; Verdu, J., *Polym. Deg. Stab.*, **60**, 275-281, 1998.]

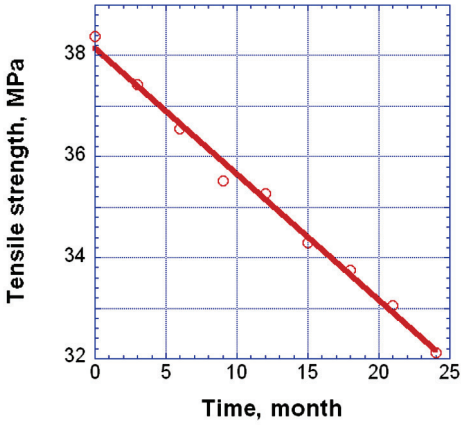


Figure 5.21. Tensile strength vs. exposure time in Algeria. [Data from Belhaneche-Bensemra, N., *J. Vinyl Additive Technol.*, **8**, 1, 45-54, 2002.]

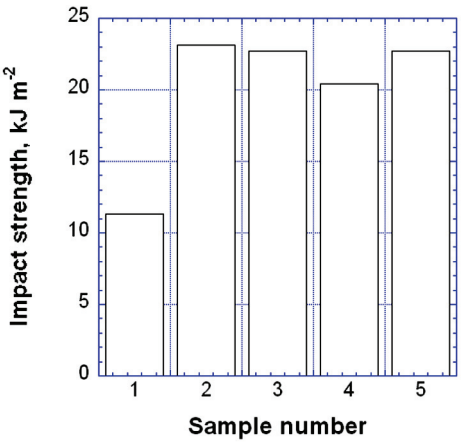


Figure 5.22. Impact strength of different samples. 1 – outdoor exposed, surface layer present; 2 – outdoor exposed, 100 µm removed; 3 – outdoor exposed, 200 µm removed; 4 – indoor exposed, surface layer present; 5 – indoor exposed, 200 µm removed. [Data from Jakubowicz, I.; Moeller, K., *Polym. Deg. Stab.*, **36**, 111-120, 1992.]

different samples taken from a 20 year old window frame exposed in Aurich, Germany. If a degraded surface layer remains before measurement, the impact strength is drastically reduced (sample 1). Samples 2 and 3 show that the degraded layer is less than 100 µm

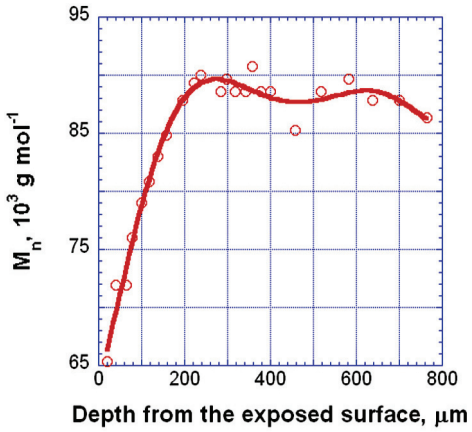


Figure 5.23. Number average molecular weight of rigid PVC after 450 h exposure in photochemical reactor at 70°C vs. depth from the exposed surface. [Data from Anton-Prinet, C.; Dubois, J.; Mur, G.; Gay, M.; Audouin, L.; Verdu, J., *Polym. Deg. Stab.*, **60**, 275-281, 1998.]

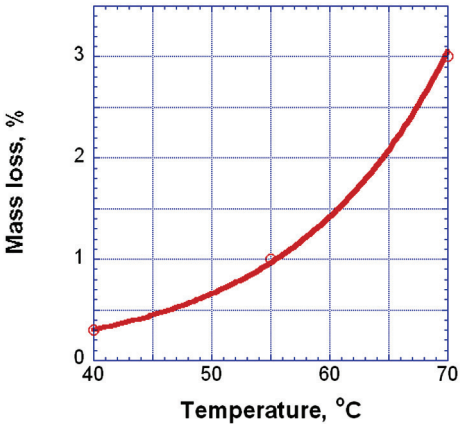


Figure 5.24. Mass loss by PVC film exposed to UV at different temperatures. [Data from Anton-Prinet, C.; Mur, G.; Gay, M.; Audouin, L.; Verdu, J., *Polym. Deg. Stab.*, **60**, 265-273, 1998.]

thick. Comparison of samples 4 and 5 shows that some surface degradation also occurs indoors.[36] Surface deterioration can be improved with proper use of thermal stabilizers with a pronounced effect on impact resistance.[55]

5.4.3 OTHER PROPERTIES

Color change and mechanical properties deterioration are the most important and easiest to detect changes which frequently impede application of material for certain purposes. There are many other manifestations of photodegradation, including molecular weight change,[27,56] change in the surface composition,[56] mass loss,[29] surface erosion,[56] gloss deterioration,[53] and change in electric properties.[57]

Figure 5.23 shows that molecular weight of surface layers is severely reduced.[25] PVC siding was exposed outdoors and its number average molecular weight was reduced by 40 to 55% in a surface layer having a thickness of 10-15 μm.[56] The degraded layer had 32% of atomic oxygen and 6% of atomic chlorine compared with no atomic oxygen and 33% of atomic chlorine in core layers.[52]

Mass loss depends not only on radiation but also on the exposure temperature. Figure 5.24 shows that the mass loss increases exponentially with increasing exposure temperature.[29] Surface erosion usually has a positive impact on color retention of PVC. PVC compounds having higher surface erosion were found to have better color retention.[53] At the same time, the gloss retention had an opposite trend.[53]

The decrease in permittivity and dielectric loss at the initial stages of degradation corresponds to a decrease in molecular mobility, which may be attributed to the formation of conjugated double bonds, as well as to a decrease in the number of mobile dipoles.[57] At

more advanced stages of degradation formation of carbonyl groups contributes to an increase in permittivity and dielectric loss.[57]

More information on physical changes can be found in a specialized monograph on material weathering.[1]

5.5 EFFECT OF ADDITIVES

5.5.1 BIOCIDES AND FUNGICIDES

Rigid PVC is resistant to microbiological attack but the addition of plasticizers and some stabilizers (e.g., epoxidized soybean oil) drastically reduces the microbiological resistance of PVC and its stabilization becomes necessary. There is no expressed concern in the available literature that biocides may influence UV stability of PVC but there are some studies which show that durability of biocides may be questionable, and these examples are discussed below.

Zinc pyrithione was used as a biocide in PVC plasticized with phthalate plasticizer and epoxidized soybean oil.[58] 150 h of QUV exposure was sufficient for material to behave as a control (without biocide). The addition of hydrotalcite slightly increased resistance to UV deterioration of biocide.[58]

Three biocides were tested in a PVC formulation containing phthalate plasticizer and epoxidized soybean oil: 10,10-oxybisphenoxarsine, OBPA, 2-n-octyl-isothiazolin-3-one, OIT, and 4,5-dichloro-2-n-octylisothiazolin- 3-one, DCOIT.[59] OBPA did not perform well in an outdoor test after 12 month of exposure. The other two biocides had good performance but DCOIT was slightly more resistant to outdoor exposure. Addition of large amounts of titanium dioxide (~20 phr) had a strong protective effect even though the formulation contained increased concentrations of the above plasticizers.[59]

Raman microscopic studies of the distribution of the fungicide Fluorfolpet show that its loss was mostly caused by leaching and diffusion of plasticizer, which was the main motoric force increasing its loss.[60]

5.5.2 FILLERS

Calcium carbonate is the most frequently used filler in PVC products. In PVC recycling, Braun[61] proposed to add 10% calcium carbonate to fortify a partially exhausted stabilizing system. This addition was expected to work by scavenging HCl evolved during thermal degradation. It was observed that calcium carbonate also participated in photochemical stabilization by scavenging HCl evolved during photodegradation.[51] Calcium chloride was detected in PVC products exposed to photodegradation.[36,53] Due to its solubility, it was being washed away by moisture and rain, leaving a porous surface layer having a thickness of 15 μm.[53] In window frames, some calcium carbonate was converted to calcium sulfate because of its reaction with sulfur dioxide, which is a common pollutant.[36] Calcium carbonate does not have screening properties and therefore it is not able to protect polymers in a manner similar to titanium dioxide.[62] Calcium carbonate, similar to other fillers and pigments, is removed from the surface by wind and rain after the surrounding polymer matrix has become sufficiently degraded.[63]

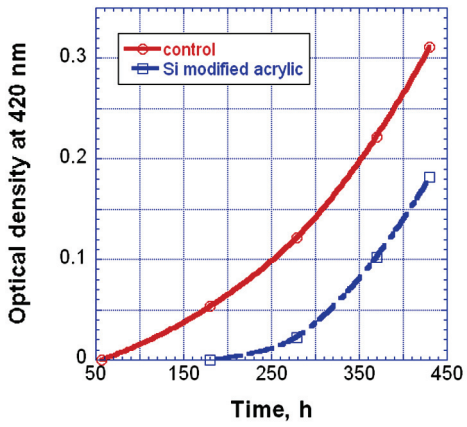


Figure 5.25. Change of color of PVC film with and without impact modifier vs. exposure time in SEPAP 12-24. [Data from Gervat, L.; Morel, P., *J. Vinyl Additive Technol.*, **2**, 1, 37-43, 1996.]

There was no loss of filler during the prolonged use of cables.[64] Mine and river sands protected PVC against photodegradation at high concentration (56 vol%).[65] Mixtures of magnesium and titanium oxide were used for window and door profile production.[66] The best weathering characteristics were obtained when the ratio of MgO to TiO_2 was 1:3. Wood fillers are used for reinforcement and to lower PVC cost. Wood fiber was found to accelerate color change of PVC.[67] Wood flour drastically increases water absorption.[68] Outdoor and laboratory exposures of PVC/pine composites caused color change, increased carbonyl concentration, and caused loss of wood particles from surface.[72] Oxidation of lignins influenced color change.[72]

Carbon black may be used as screening agents in protection of PVC materials.[70]

In combination of two fillers, photo-inert calcium carbonate nanoparticles hindered the photodegradation of PVC, whereas the photoactive zinc oxide nanoparticles accelerated the photodegradation of poly(vinyl chloride).[71] The ZnO nanoparticles also favored the crosslinking reaction of the dehydrochlorinated poly(vinyl chloride).[71]

More information on the effect of fillers can be found in the monographs on the subject of weathering and fillers.[1,69] In some polymers, silica fillers were found to absorb stabilizers and therefore reduce polymer stability. A similar contribution does not exist for PVC, which may be due to inadequate research.

5.5.3 FLAME RETARDANTS

There is very limited information on flame retardants' effect on PVC photostability. It is known that chloroparaffins, which are seldom used now, have a detrimental effect on PVC photostability because they are themselves unstable and produce radicals which initiate PVC degradation.[73] Similar is the case of bromine flame retardants, which on UV exposure produce bromine radicals, which again abstract polymer hydrogen.[1]

5.5.4 IMPACT MODIFIERS

In the past there were issues with impact modification related to the use of polybutadiene or its copolymers, which were not UV resistant because of their vulnerable double bonds, but this is generally a past issue because for outdoor applications, acrylic impact modifiers are now in common use.

Acrylic modifiers were found[51,74] to increase color stability (Figure 5.25). It is pertinent that substantial improvement in color stability can be obtained with acrylic impact modifiers. There are different types of acrylic modifiers and they do not offer the same

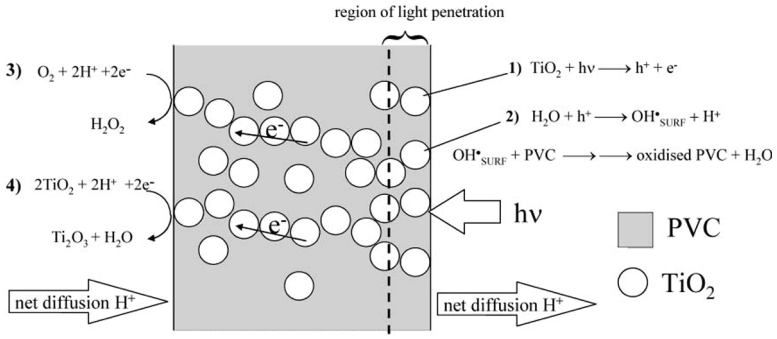

region of light penetration
3) $O_2 + 2H^+ + 2e^-$
H_2O_2
4) $2TiO_2 + 2H^+ + 2e^-$
$Ti_2O_3 + H_2O$
1) $TiO_2 + h\nu \longrightarrow h^+ + e^-$
2) $H_2O + h^+ \longrightarrow OH^{\bullet}_{SURF} + H^+$
$OH^{\bullet}_{SURF}$ + PVC ⟶ ⟶ oxidised PVC + H_2O
hν
PVC
TiO_2
net diffusion H^+
net diffusion H^+

Figure 5.26. Schematic diagram of photoresponse mechanism in TiO_2 pigmented PVC membranes. [Adapted, by permission, from Belghazi, A.; Bohm, S.; Worsley, D. A.; McMurray, H. N., *Z. Physik. Chem*., **219**, 11, 1539-1546, 2005.]

color improvement, but they are all generally useful in photostabilization of PVC products.

5.5.5 LUBRICANTS

Lubricants belong to the group of chemicals which are at least as stable as PVC and they are usually used in small concentrations.[51,65] The available literature does not implicate these products in any direct influence on PVC photostability. They may affect initial color of the product because they have been used at too low a concentration or in the wrong combination and material was thermally degraded. They also may affect surface and mechanical properties because the wrong type and too large concentrations were used during processing.[65] Lubricants have an indirect influence on PVC photostability because their performance controls thermal damage of PVC, which is very essential for its photostability.[51]

5.5.6 PIGMENTS AND COLORANTS

5.5.6.1 Titanium dioxide

Titanium dioxide is probably the most essential additive for PVC materials which are designed to perform outdoors. The reason is that titanium dioxide participates in photolytic processes that are essential for color stabilization of PVC. Many polymers use titanium dioxide for coloring but outdoor grades of PVC use exceptional quantities of titanium dioxide to prevent change of color. Let's begin with a description of its role from a state of the art understanding of its mechanism of action. Figure 5.26 shows a schematic diagram of its action based on the studies of photochemically driven charge transport across a PVC membrane pigmented with titanium dioxide.[75]

Titanium dioxide is a n-type semiconductor with a band gap energy, E_{bg}, of approximately 3.2 eV. The illumination with light of $h\nu > E_{bg}$ generates a non-equilibrium electron, e^-, and hole, h^+, pairs (see equation 1 on diagram).[75] The energy greater than 3.2 eV is obtained by absorption of radiation of wavelength below 387 nm.[76]

The low diffusion length of h^+ (0.1–1 μm in a single crystal TiO_2) constrains the photoanodic process (equations 2 in Figure 5.26) proximal to the site of photoexcitation (near

the illuminated surface). Electrons have a sufficiently long lifetime and mobility and therefore the cathodic processes (equations 3 and 4 in Figure 5.26) can occur on both sides of the membrane.[75] This shows that processes on the exposed side are controlled by penetration of radiation (therefore there is limited thickness of the reactions 1 and 2) and also by the presence of oxygen and water. The processes on the reverse side of the sample are controlled by oxygen diffusion and reaction (this restricts their penetration into the depth of the backside of the sample) and presence of water.

These are very important findings put in the form of a sequential mechanisms which explain why there are 3 essential ingredients of TiO_2 performance: radiation, water, and oxygen. If irradiation was performed without oxygen, a blue coloration of membrane occurred which was rapidly bleached on contact with air. The blue color is consistent with accumulated e^- reducing Ti^{IV} to Ti^{III} through a process described by equation for 4 in Figure 5.26.[75]

In the previous explanations of color formation in the transparent samples we have used two premises that oxygen is present on both sides of the sample and radiation penetrates the entire sample which explains why concentration of carbonyl groups has a parabolic character with high concentrations of carbonyls on surfaces and none at the core. Sometimes these parabolas are skewed, which is explained by extensive absorption of radiation by already formed polyenes. But in the case of material which contains light absorbing pigments such as TiO_2, radiation is absorbed more extensively. Gardette and Lemaire[19] show that the oxidation depth profile is limited to the first 80 μm from the exposed side of a sample containing 8% TiO_2, whereas in a non-pigmented sample it extended to 150 μm.[19] In the studies of thick samples it was discovered[19] that the polyenes with the shortest conjugation lengths, whose absorbance is below 400 nm, are protected by the screen effect of the pigment. These short polyenes were accumulating in the polymeric matrix. This seems to support the existence of a process given by equation 3 in Figure 5.26, which means that polyenes are formed in the layers deeper than the penetration of radiation because electrons and oxygen are able to propagate oxidation processes without light. The membranes used in the experiment discussed above were very thin (25 μm); it is therefore not possible to use this experiment to determine the depth of changes nor there are other data available which may help to understand this part of the mechanism.

Titanium dioxide properties are very important for the expected outcome. A photoactivity test for TiO_2 was developed which provides data on pigment performance based on carbon dioxide evolution from irradiated films, which helps to determine the photoactivity index.[77] The higher the pigment photoactivity, the higher the rate of photocatalytically generated carbon dioxide formation.[77] Pigments which are used for exterior coatings have a very low photoactivity index (below 1%). They are rutile TiO_2 grades having Al/Si and Al/Si/Zr coatings. This index, although not used in PVC studies, may help fine-tuning of titanium oxide grades to the requirements of PVC protection.

Figure 5.27 shows PVC film containing TiO_2 after exposure in Japan for 20 days.[76] The film was produced to study the potential of use of solar energy for mineralization of PVC waste. For this reason, catalytic TiO_2 (Degussa P-25: 83% anatase and 17% rutile) was used to accelerate the process of degradation. Although the degradation rate is exag-

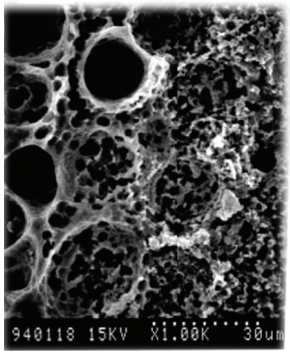


Figure 5.27. PVC film exposed for 20 days in Japan. [Adapted, by permission, from Horikoshi, S.; Serpone, N.; Hisamatsu, Y.; Hidaka, H., *Environ. Sci. Technol.*, **32**, 24, 4010-4016, 1998.]

gerated compared with typical PVC products, the process mechanism is correctly illustrated. The SEM micrograph shows regular spherical (up to cylindrical) holes which were burned out of the material. The smaller holes contained titanium dioxide pigment which was lost from the surface.

This is part of the mechanism of the so-called surface renewal which contributes to the color retention by PVC articles. From the composition side, the degradation rate depends on the crystalline structure of titanium dioxide (anatase or rutile) and surface doping.[78] The doping of TiO_2 (rutile) with Al(III), Cr(III), Mn(II), Si(IV), V(V) reduces the photoactivity of the pigment, while doping by Mo(V) or W(V) enhances its photoactivity; the results obtained from carbonyl index measurements confirm this effect. The greatest protection to PVC film was offered by TiO_2 coated with Al_2O_3 or SiO_2.[78] The photoactivity of doped TiO_2 is a complex function of dopant concentration, the energy levels of the dopants in the TiO_2 lattice, their d electronic configuration and their local distribution.[78] Photoactivity is also linked to other factors such as crystal type, particle size distribution, and surface area.[78]

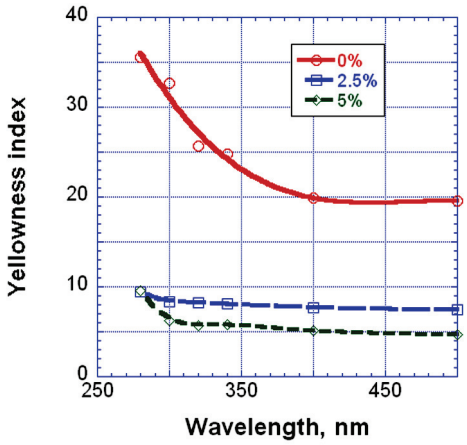


Figure 5.28. Yellowness index vs. wavelength of radiation for PVC samples containing 0, 2.5, and 5% TiO_2. [Data from Andrady, A. L.; Torikai, A.; Fueki, K., *J. Appl. Polym. Sci.*, **37**, 935-946, 1989.]

Water is a very prominent factor in titanium oxide-assisted photodegradation. This is very well known from laboratory studies which indicate that the success of these studies depends on maintenance of a proper level of humidity and simulation of rain. Real *et al.*[35] show that use of a Weather-Ometer without water spray did not give a good correlation with natural exposure in Lisbon but a good correlation was obtained when a typical cycle (including water spray) was applied.[35]

Figure 5.28 shows that color stability of PVC with and without TiO_2 is completely different. Without TiO_2, the sample degrades when exposed to radiation up to 340 nm (yellowness index of unexposed control was 21.8). Radiation above this wavelength (400 and 500 nm) causes photobleaching. In the case of samples containing TiO_2, wavelengths of 280, 300, 320, and 340 nm also caused some discoloration (yellowness index of unexposed samples is 7.92 and 5.19 for 2.5% and 5% TiO_2, respectively) but the discoloration is small compared with a sample without pigment. Photobleaching seems to be related to polymer and radiation wavelength (it is more efficient at 400 and 500 nm). Sub-

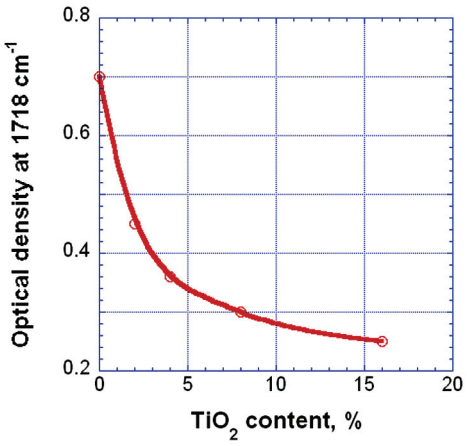


Figure 5.29. Carbonyl absorption vs. TiO_2 content. 175 h exposure in SEPAP 12-24. [Data from Gardette, J.-L.; Lemaire, J., *Polym. Deg. Stab.*, **16**, 147-158, 1986.]

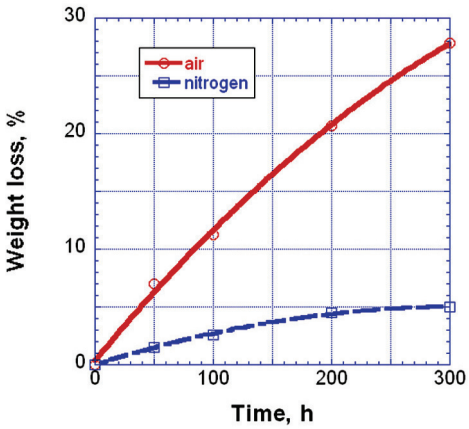


Figure 5.30. Weight loss during UV exposure in nitrogen and air vs. exposure time. [Data from Cho, S.; Choi, W., *J. Photochem. Photobiol., A: Chem.*, **143**, 221-228, 2001.]

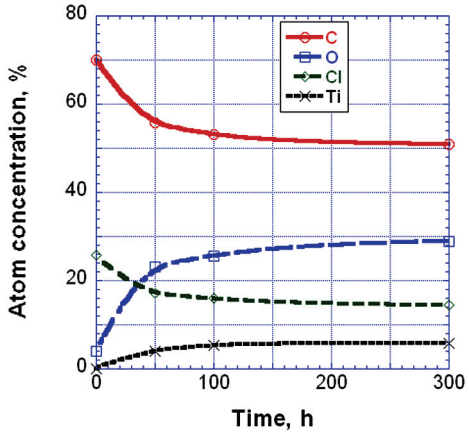


Figure 5.31. XPS concentration of surface atoms on PVC sample vs. exposure time. [Data from Cho, S.; Choi, W., *J. Photochem. Photobiol., A: Chem.*, **143**, 221-228, 2001.]

stantially whiter color with TiO_2 is a combination of pigment color, its screening effect, and oxidation of polyenes.

Figure 5.29 shows the effect of TiO_2 concentration on PVC stability. Carbonyl content exponentially decreases with concentration of TiO_2 increasing. This shows the reason why some formulations contain a very high load of pigment.

Figure 5.30 shows that oxygen presence during photodegradation accelerates weight loss. Figure 5.31 shows that the concentrations of carbon and chlorine from PVC are decreasing on the sample surface, whereas concentrations of oxygen and TiO_2 increase, as should be expected from the process in which a surface is refreshed (and color retained) because organic material on the surface is being degraded, and inorganic material is gradually removed by wind and rain.

Crystallinity of PVC without TiO_2 increased noticeably on exposure to accelerated weathering, whereas no significant change was observed when TiO_2 was present.[80] Chain scission and crosslinking reactions occurred in PVC without TiO_2, whereas only chain scission occurred in PVC containing TiO_2.[80] The chain scissions in PVC without TiO_2

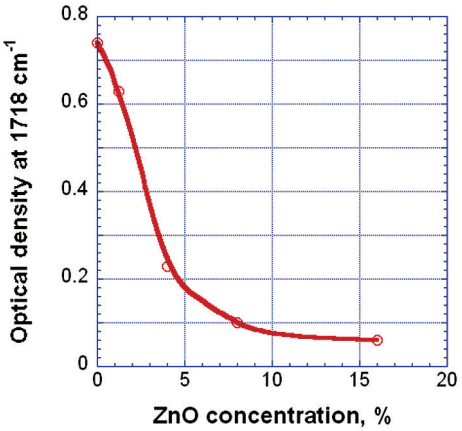


Figure 5.32. Carbonyl absorption vs. ZnO content. 175 h exposure in SEPAP 12-24. [Data from Gardette, J.-L.; Lemaire, J., *Polym. Deg. Stab.*, **16**, 147-158, 1986.]

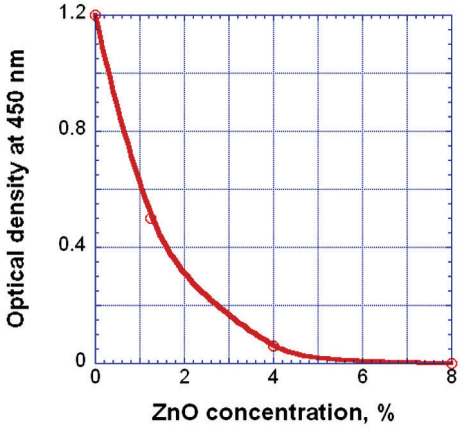


Figure 5.33. Discoloration vs. ZnO content. 100 h exposure in SEPAP 12-24. [Data from Gardette, J.-L.; Lemaire, J., *Polym. Deg. Stab.*, **16**, 147-158, 1986.]

were initiated earlier than in PVC with TiO_2, producing shorter and more mobile chains that underwent secondary crystallization.[80]

The presence of dibasic lead phosphate when associated with a specific titania pigment caused pinking.[81] The presence of water was essential for pinking reaction.[81] PVC containing Ca/Zn stabilizers remained white regardless of the titanium dioxide grade used.[81]

5.5.6.2 Zinc oxide

Zinc oxide is a white pigment, foaming catalyst (activator), and component of smoke suppressant. Figure 5.32 shows its effect on carbonyl formation. Conditions of the experiment are the same as for TiO_2 (Figure 5.29).[20] It is noticeable that less carbonyl is formed with ZnO as compared with TiO_2, especially at higher pigment concentrations. This is explained by a better dispersion and thus better screening properties of ZnO.[22] Figure 5.33 shows that ZnO is very effective in preventing discoloration of PVC.

On the other hand, zinc oxide was found to catalyze PVC degradation and it is even proposed for use in photocatalytic decomposition of PVC wastes.[82-84] The degradation products of PVC degradation in presence of ZnO were aldehydes, carboxylic acid and carbon dioxide.[82] Dye-sensitization, using Eosin Y, enhanced degradation of PVC.[83] In addition to carbon dioxide, the degradation products included aldehyde, ketone, and carboxylic acid functional groups.[83] Combination of ZnO and TiO_2 substantially enhances photocatalytic activity of pigments.[84]

5.5.6.3 Iron-containing pigments

Iron is a known degradant in photocatalytic processes. Many pigments contain iron, therefore there is interest in their performance in outdoor formulation. Only limited studies can be found.[85-86] Peake[86] reported studies on 17 pigments which contain from 7.5 to 69.9% total iron and from 0.12 to 66% extractable iron and concluded that there is a correlation

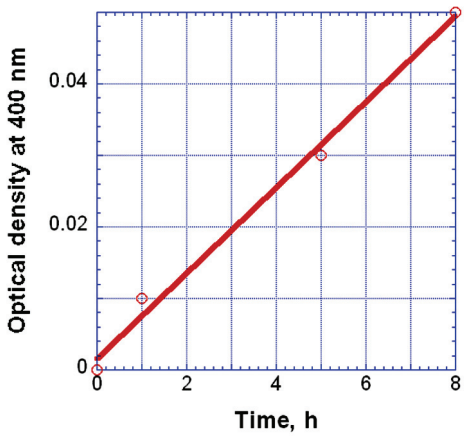


Figure 5.34. DOP discoloration vs. exposure time to UV at 300 nm. [Data from Hollande, S.; Laurent, J.-L., *Polym. Deg. Stab.*, **55**, 2, 141-145, 1997.]

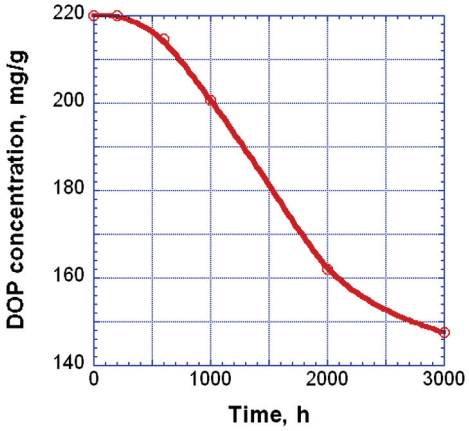


Figure 5.35. DOP concentration vs. time of exposure in WEL-SUN-DC. [Adapted, by permission, from Ito, M.; Nagai, K., Polym. Deg. Stab., **92**, 2, 260-270, 2007.]

between extractable iron and the weathering performance of rigid PVC containing these pigments.[86] These comments are based on color changes of a test formulation containing 2% pigment and 8% titanium dioxide after 2 year Florida exposure.[86] In another study,[85] a color shift was reported during storage of samples with various pigments, but not in the case of iron containing pigment.

5.5.7 PLASTICIZERS

Plasticizers play an important role in semirigid and soft PVC grades and their influence extends to photodegradation processes. Plasticizer influences include:

- absorption of UV radiation (screening effect),
- their own degradation,
- migration, evaporation, and extraction loss,
- effect on oxygen permeability,
- formation of carbonyl groups.

Photodegradation studies at 257 nm (radiation not available in sunlight) show that 96% of radiation is absorbed by plasticizer and only 4% by PVC.[87] In the range of UV radiation available in sunrays, plasticizers absorb effectively in the 300-330 nm range which is strongly damaging to PVC.[22,88] These two observations show that plasticizers screen a substantial part of radiation by which they prevent PVC degradation. It was observed that the number of radicals decreased with increasing concentration of dibutyl sebacate.[43]

Products of plasticizer degradation contribute to discoloration (Figure 5.34). The plasticized PVC films yellow to a color darker than the sum of the PVC and the plasticizer discolorations.[38] Plasticizers were also found to produce radicals which contribute to PVC photodegradation.[38,43]

Figure 5.35 shows that plasticizer is lost during exposure.[63] The loss of plasticizer and filler makes a surface porous, which increases the potential for further degradation because it increases oxygen diffusion.[90] It was observed that the leaching of plasticizer to oils and solvents is reduced when material is exposed to UV radiation.[91]

The permeability to oxygen of plasticized PVC films, having 23% dioctyl phthalate, is approximately 20 times higher than for rigid PVC (0.70×10^{-10} cm^3 s^{-1} cm^{-1} Hg versus 0.03×10^{-10} cm^3 s^{-1} cm^{-1} Hg for rigid PVC).[92]

PVC, isolated from plasticizer after irradiation at 257 nm (not available in sun radiation), was found to contain phthalate fragments attached to the polymer.[87] Two instruments were compared in studies of plasticized PVC. A Weather-Ometer predicted outdoor performance, whereas degradation of samples under fluorescent lamp radiation (QUV) did not correlate with outdoor degradation.[93] PVC sheets were irradiated under different conditions, as follows:

1. (52.5 $\mu W/cm^2$)
2. (0.45 mW/cm^2)
3. (8.3 mW/cm^2)

The first two exhibited considerable toxicity in cytotoxicity tests and chromosome aberration tests due to the generation of DEHP oxidants, but no toxicity was detected in the PVC sheet irradiated under the last condition.[94]

5.5.8 POLYMER BLENDS

PVC forms commercial weather-resistant blends (Enplex and Kydex).[1,95] A few experimental blends were studied, including PVC/NBR, PVC/EVA, PVC/PS, PVS/SAN, PVC/PPy, PVC/PANI, and PVC/acrylic.[74,95-97] The only essential information from these studies regards PVC/PPy and PVC/PANI blends which, when exposed to UV radiation, benefit from PVC degradation because evolved HCl dopes conductive polymers which render their conductivities to the blend. The blend without PVC degradation would have been substantially less conductive.[96-97]

5.5.9 SOLVENTS

Commercial processing of PVC does not require solvents and they are not knowingly used by quality concerned processors. It is possible that some manufacturers of additives use solvents to homogenize their products but this is rare and should not happen at all.

In laboratory studies, solvents are frequently used for analytical purposes and, what is more detrimental, for preparation of specimens for degradation studies or studies in liquid form. These practices may lead to misconceptions for two essential reasons. First of all, solvents entrapped in polymer film may act as sensitizers and produce radicals which have nothing to do with PVC degraded without the presence of solvents. Such circumstances will alter the chemistry and kinetics of photodegradation. Tetrahydrofuran is a classical example, reported long ago by Rabek *et al*.[98] It is also true that proper removal of tetrahydrofuran may give specimens which degrade more slowly than specimens prepared by heating as was found by Andrady *et al*.[9] However, the risk is not worth the effect because PVC is fused by heating and the history of sample preparation important for the results of photodegradation should agree with industrial processes.

There is still another reason for not using solvents in laboratory and industry. Gardette and Lemaire remind us that solvents increase segmental mobility and may support rotation of the C–C bond, which may change the mechanism of degradation (especially propagation kinetics) as was discussed in this and previous chapters.[22] Also, solvent acting as plasticizer may contribute to the redistribution of polyenes (isomerization).

5.5.10 STABILIZERS

The influence of stabilizers on these and other properties of PVC are discussed in full in Chapter 11 and their discussion is omitted here.

5.5.11 PVC MODIFICATION

Carboxylated PVC, having 1.8% of carboxyl groups, showed accelerated photodegradation and crosslinking and decelerated photodehydrochlorination.[99]

The reaction of poly(vinyl chloride) with iodide, hydroxide, azide, and thiocyanate as nucleophiles in ethylene glycol resulted in the substitution of Cl by nucleofiles in addition to the elimination of HCl.[100] The dehydrochlorination rate of these substitutes was increased.[100]

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6

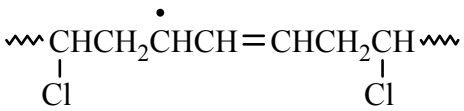
Principles of Degradation by γ-Radiation

6.1 THE REASONS FOR POLYMER INSTABILITY

UV radiation in the range from 290 to 380 nm has a quantum energy in the range of 4.3 to 3.3 eV, whereas the average energy of γ-rays emitted by ^{60}Co equals 1.25 MeV. Comparison of these values shows a great energy disparity between both forms of radiation. The energy delivered by γ-rays is much higher than the energy necessary for any organic bond to be dissociated; they can directly cause formation of double radicals, which is not possible with UV rays. The mechanism of radiation absorption is also different compared with UV radiation. In the case of UV only specific radiation can be absorbed; therefore, absorption is limited by polymer structure. In the case of γ-radiation, absorption depends only on material density, i.e., the number of atoms in material volume, since radiation energy exceeds the order of magnitude of bond energy and ionization energy. Also, the ability to penetrate the entire thickness of a material is a distinctive feature of γ-radiation. UV photolysis is concentrated mainly on the material surface, while high-energy radiation acts on the full volume of material. From this brief comparison, we can see that the changes expected may vary from those caused by thermal degradation and UV photolysis.

6.2 MECHANISMS

Similar to other decomposition processes the dehydrochlorination reaction is also typical of γ-radiation degradative process. ESR spectrum of γ-irradiated PVC sample contained a septet line-spectrum attributed to the following radical:[1]



which at higher temperatures was converted to a polyene radical.[2] Irradiated PVC generates HCl continuously during storage at 353K.[3] Samples of PVC reduced with tri-n-butyltin hydride, according to the procedure of Starnes,[4] when irradiated with ^{60}Co γ-rays, produced low molecular weight alkanes and alkenes.[5] This may indicate that branches react first under γ-radiation. Under inert-gas atmosphere, alkyl radicals are formed,[6] which lead to a decrease in the molecular weight of the polymer. The radicals are transformed to peroxyradicals[7,8] when a sample, on irradiation, is exposed to air. Oriented films exhibited an increase in carbonyl index after γ-irradiation, which was explained by better oxygen

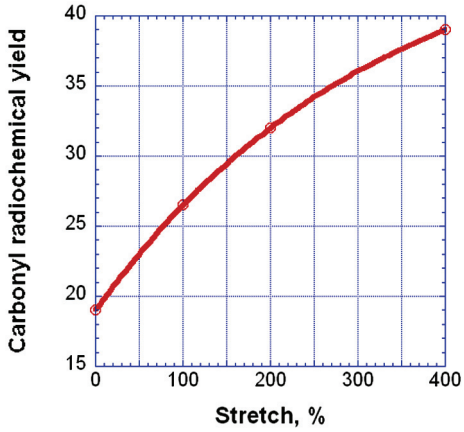


Figure 6.1. Carbonyl radiochemical yields in samples exposed to 76 kGy vs. sample elongation. [Data from Thominette, F.; Verdu, J., *Polym. Deg. Stab.*, **36**, 59-63, 1992.]

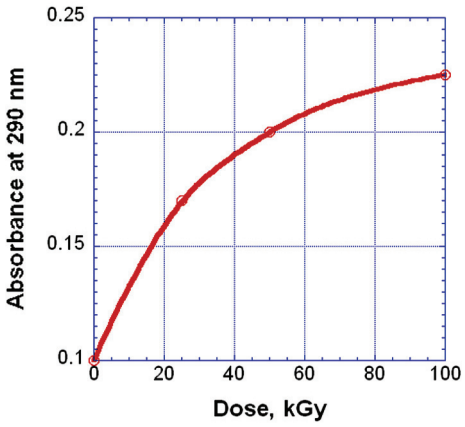
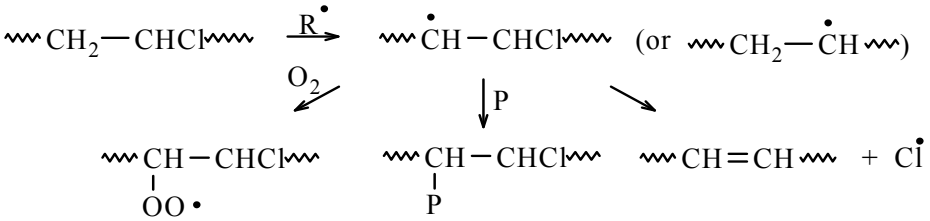


Figure 6.2. Absorbance at 290 nm vs. dose for unstabilized PVC sample. [Data from Naimian, F., *Nuclear Instruments Methods in Phys. Res., Sec. B: Beam Interactions with Materials and Atoms*, **151**, 467-470, 1999.]

solubility in drawn PVC films. A study[9] confirmed observations (Figure 6.1) but gave a different explanation which suggests that orientation favors chain conformations in which hydrogen abstraction from methylene groups is easier.[9]

Irradiation in the presence of air causes more chain scissions[10] than that in inert atmosphere, which facilitates crosslinking.[11]

Baccaro *et.al.*[12] show that samples exposed to radiation change color to dark yellow, ESR signal increases (radical formation), and oxidation increases (increased carbonyl absorption). UV absorption also increases with radiation dose increasing (Figure 6.2).[13] These and other studies suggest the following mechanism of degradation:



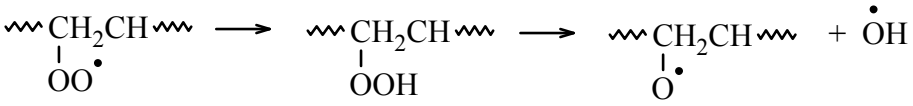
The basic features of the mechanism include abstraction of either chlorine or hydrogen radical, followed by oxidation (with potential chain scission), recombination with another radical (P can be another radical chain which results with crosslinking), and dehydrochlorination with formation of double bonds. Free radicals created by room temperature irradiation in solid polymers are immobilized and may remain trapped for a considerable length of time.[14] Those radicals are responsible for post-irradiation "aging" of many polymers and thus of PVC.[14]

Large doses of radiation applied to PVC samples showed that the amount of chlorine decrease from 59.57% in the original PVC to 50% after 10 MGy, to 18% after 20 MGy and to 5.8% after 200MGy.[15] The irradiation caused formation of a relatively large wire-like (fibrile) structures. The interplanar distance of these structures was 0.59 nm and length of 200 nm.[15] This shows that degradation can ultimately proceed to formation of graphite-like structures.[15]

6.3 KINETICS

Considering the very high energy of radiation compared with the energy required for dissociation of a bond in PVC, it can be assumed that radical processes can be initiated at any carbon atom. The labile groups, which play a role in initiation of thermal degradation of PVC, do not influence kinetics of degradative changes on exposure to γ-radiation.

Propagation is a process in which hydroperoxides dissociate forming two radicals:[16]



The hydroxyl radical abstracts hydrogen from the neighboring site and propagates degradative reactions.

Termination occurs by coupling or disproportionation in a cage reaction. Elevated temperature of the process increases mobility of macromolecules and promote propagation and escape from the cage, which promotes β-scission processes and formation of radicals.[16]

6.4 RESULTS

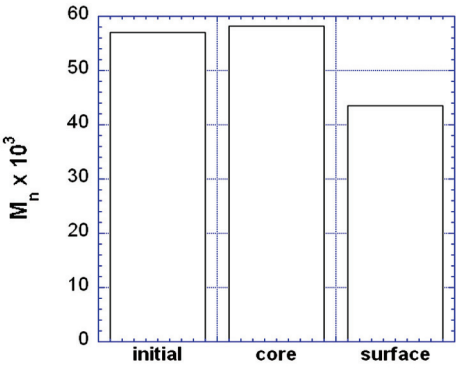


Figure 6.3. Molecular weight of sample before and after exposure to 165 kGy. [Data from Thominette, F.; Metzger, G.; Dalle, B.; Verdu, J., *Eur. Polym. J.*, **27**, 1, 55-59, 1991.]

Figure 6.3 shows that chain scission has a higher probability on a surface where oxygen is readily available, but crosslinking more likely occurs at the sample core where the energy of radiation is transferred but oxygen is not readily available due to a slow diffusion process.[16] Colombani *et al.*[14] noted that it is very difficult to remove oxygen from PVC samples. Samples were kept under vacuum for 24 h, then under helium during exposure to γ-radiation. ESR measurements confirmed the presence of some oxygen containing radicals.

The major use of γ-irradiation is sterilization of medical devices and food packaging. It is thus important for quality purposes that sterilization does not affect

esthetic properties and mechanical performance of sterilized goods. If conditions of sterilization are properly selected and PVC materials are adequately stabilized, there is no effect of irradiation on tensile strength and elongation.[17,18] Sequential exposure of cable to heat (45 to 110°C) and irradiation decreased elongation of cables used in nuclear plants.[19] Reprocessing of medical vinyl compounds (addition of 20% regrind) did not affect tensile strength and elongation of extruded and injection molded goods.[20]

Ultrasonic wave velocity and hardness of PVC samples exposed to 300 Mrad doses were decreased.[21] Thermal expansion coefficient changes depend on the temperature at which irradiation occurs and the dose of radiation.[22] At temperatures from 10 to 110K, the coefficient of thermal expansion decreases with a dose of irradiation increasing. The opposite is the relationship on irradiation at 110 to 340K. At lower temperature range, crosslinking prevails, and at the higher temperature range, chain scission is more common. The thermal expansion of the solid whose atoms/molecules are held by van der Waal's forces is about two orders of magnitude greater than that of a covalently bonded solid. Thus the relative increase in the van der Waal's bonds caused by the chain scission of the polymer chain by irradiation is responsible for an increase in thermal expansion coefficient with radiation dose.[22] Crystalline order in PVC is destroyed by irradiation.[7]

Raising temperature during irradiation with typical sterilization doses increases the HCl production by a factor of about 1.3.[23] Relative humidity during irradiation does not seem to play essential role in changing dehydrochlorination rate.[23]

The bi-oriented PVC can withstand high β- and γ-radiation doses (up to 100 kGy) without significant degradation in its mechanical properties.[24] Bi-orientation of polymer chains in the bulk of material is not affected even by much higher doses (250 kGy).[24]

γ-rays interaction parameters with six polymer (including polyamide, poly(ethylene terephthalate), polymethylmethacrylate, and PVC) and plastic materials were investigated to establish their shielding properties.[25] PVC was found to have the best shielding capabilities in the energy range from 10 to 110 keV.[25]

More information on property changes can be found in the next section.

6.5 EFFECT OF ADDITIVES

6.5.1 PLASTICIZERS

Didecyl phthalate was found to increase probability of chain scission (Figure 6.4). The increased rate of chain scission is explained by increased diffusion of oxygen.[16] Plasticizer was slightly decreasing the rate of crosslinking because of increased chain mobility which favors recombination.[16] In the same study it was also observed that plasticizer was changing its chemical structure by dimer formation, according to the following equation:[16]

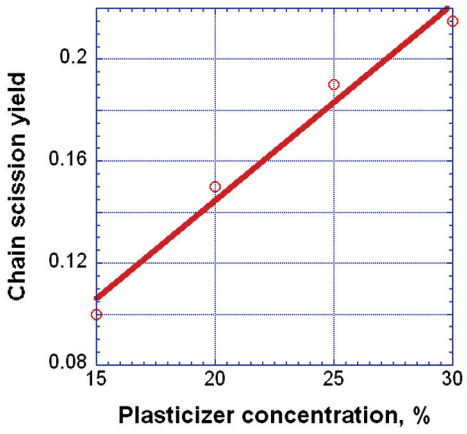


Figure 6.4. Radiochemical yield of chain scission vs. concentration of didecyl phthalate. [Data from Thominette, F.; Metzger, G.; Dalle, B.; Verdu, J., *Eur. Polym. J.*, **27**, 1, 55-59, 1991.]

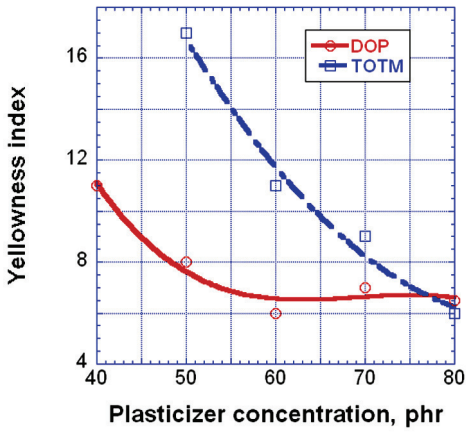
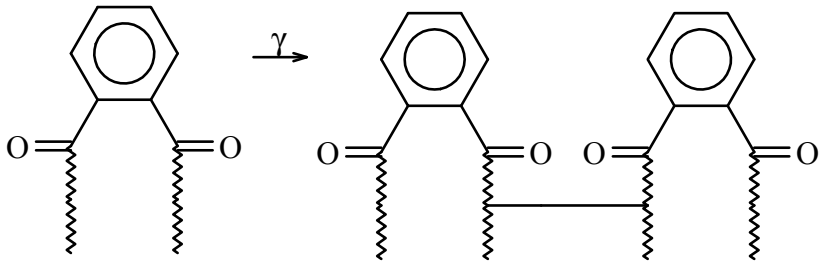
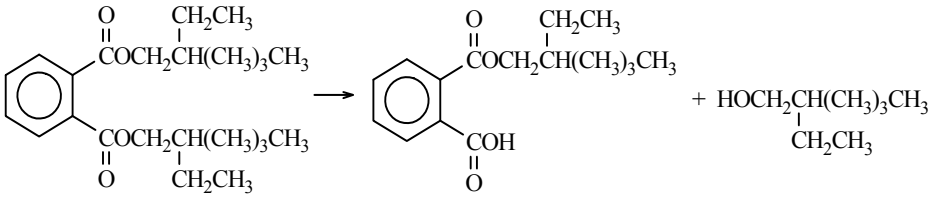


Figure 6.5. Yellowness index of PVC samples irradiated with 4 Mrad dose vs. plasticizer concentration. DOP – dioctyl phthalate, TOTM – trioctyl trimellitate. [Data from Khang, G.; Kong, C.-S.; Rhee, J. M.; Lee, H. B., *Bio-Medical Mater. Eng.*, **12**, 135-147, 2002.]



Plasticizer hydrolysis was found to take place during sterilization of PVC medical devices:[26]



The formation of monoester is confirmed without any doubt but the concentrations produced are insignificant for human health.[26]

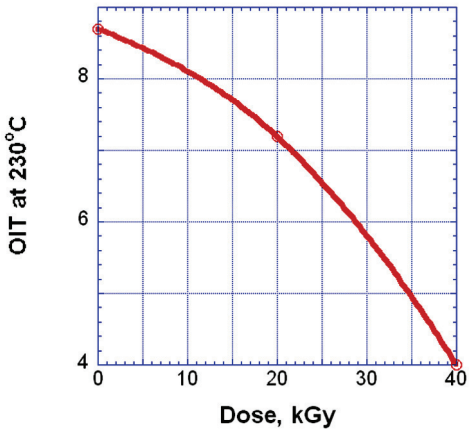


Figure 6.6. Oxidative induction time of PVC samples vs. dose. [Data from Shang, S.; Ling, M. T. K.; Westphal, S. P.; Woo, L., *J. Vinyl Additive Technol.*, **4**, 1, 60-64, 1998.]

Figure 6.5 shows the effect of γ-irradiation on color change. Both plasticizers help to preserve color.[27] This is in agreement with data in Figure 6.4 considering that color preservation is caused by oxidation of double bonds due to better oxygen diffusion. The data obtained for these samples show that molecular weight does not change substantially but polydispersity increases, which suggests that both crosslinking and chain scission processes occur.[27] In several other studies,[28-30] plasticizer concentration increase always improves color retention. For these reasons, plasticizers are considered in these applications to be additives which protect against material degradation.

The effect of plasticizers on molecular weight, tensile strength, and elongation cannot be univocally described because these properties are affected in a complex way. In the case of molecular weight, two processes occur simultaneously: crosslinking and chain scission, which means that even if molecular weight does not change during irradiation, polymer does not remain the same as before irradiation. In the case of mechanical properties, plasticizers play some role in preservation of original mechanical performance, but the most important influence comes from thermal and UV stabilizers. Most available data are for full formulations therefore data are affected by all components of the mixture.

The overall thermal stability of plasticized PVC measured by oxidative induction time decreases on γ-irradiation (Figure 6.6).[31] Compared with PE and PP, PVC was found to be the most stable polymer during γ-sterilization of medical packaging.

Food-grade PVC film containing 28.3% dioctyl adipate, DOA, plasticizer was used to wrap chicken meat samples. Samples were irradiated with γ-radiation at doses equal to 4 kGy and 9 kGy corresponding to "cold pasteurization". Results showed no statistically significant differences in migrated amounts of DOA between irradiated and non-irradiated samples.[32]

Treatment of poly(vinyl chloride) cling film with γ-rays (doses up to 25 kGy) causes chain scission and disruption of some polymer–plasticiser associations.[33] This is followed by an increase in matrix free volume and by increase of plasticizer migration.[33]

Organic products leaching from PVC exposed to high doses of γ-irradiation are plasticizers and their degradation products.[34] The main leaching products are phthalic ions formed by the hydrolysis of phthalic esters in alkaline leaching solution.[34] Figure 6.7 shows that diffusion coefficients of leaching products diminish with radiation dose increasing.[34] This can be explained by crosslinking and grafting reactions, which cause material microstructure to become less permeable, slowing down migration.[34]

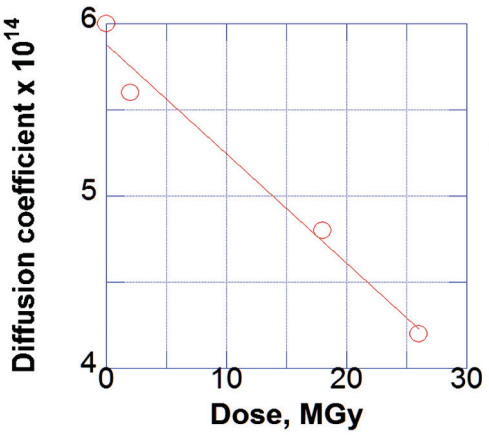


Figure 6.7. Diffusion coefficient of migrating products from γ-irradiated materials vs. radiation dose. [Data from Colombani, J.; Herbette, G.; Rossi, C., Joussot-Dubien, C.; Labed, V.; Gilardi, T., *J. Appl. Polym. Sci*., **112**, 1372-77, 2009.]

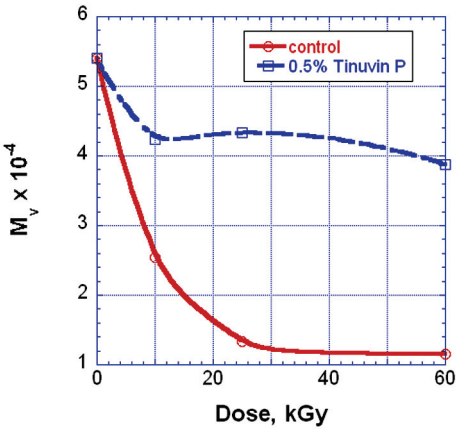


Figure 6.8. Molecular weight of PVC vs. irradiation dose. [Data from Vinhas, G. M.; Maior, R. M. S.; De Almeida, Y. M. B., *Polym. Deg. Stab*., **83**, 3, 429-433, 2004.]

It was found that migration of di(2-ethylhexyl) phthalate decreased with dose of radiation increased in the range of 0-50 kGy (γ-rays sterilization of medical devices uses at least 20-25 kGy).[35] At the same time migration of its degradation product (mono(2-ethylhexyl) phthalate) increased.[35]

6.5.2 FILLERS

Some fillers, such as zeolites, other metal silicates, calcium carbonate, barium sulfate, magnesium oxide, and zinc oxide were reported to inhibit dehydrochlorination and crosslinking.[36] Addition of calcium carbonate to a reactive mixture containing trifunctional acrylic inhibits the effectiveness of the crosslinking process by γ-irradiation.[37]

PVC containing mixture of copper chloride and potassium iodide showed no significant degradation on exposure to γ-irradiation.[38] Without this addition main chain scission was observed which did not occur with filler.[38] Also mechanical and thermal properties of PVC were improved.[38]

6.5.3 STABILIZERS

Many thermal stabilizers have been found useful in preserving the color of PVC products exposed to γ-radiation.[36] These include calcium/zinc metal carboxylates, sulfur containing tin stabilizers, alkyl mercaptans, epoxidized soybeans oil, and phenolic antioxidants.[36] Also, UV absorbers and organophosphites were found to prevent degradation on exposure to γ-radiation.[36] Figure 6.8 shows that Tinuvin P decreases the rate of molecular weight change.[39]

Koch[40] applied γ-radiolysis to monitor the lauric acid from thermal stabilizer substitution into the PVC chain by measuring undecane evolvement. Other papers[41-43] have reported that epoxy stabilizers act during γ-irradiation in a similar manner to what they do in thermal degradation.

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7

Degradation by Other Forms of Radiation

7.1 ARGON PLASMA

Wettability, adhesion, adsorption, printability, chemical reactivity, and sensitivity to light are changed by treatment with argon plasma.[1] A biocompatibility of medical devices and prostheses with living tissues is improved by a treatment with argon plasma.

The main reactions occurring on polymer surface in plasma are etching, cleaning, crosslinking, grafting, addition, substitution, and formation of functional groups. The type of modification depends on the presence of active species in plasma.

Remote plasma is used in studies included in this section. In remote plasma treatment the different lifespans of various active particles such as electrons, ions, and free radicals are used to separate them at a plasma field and attain super-pure and concentrated free radicals at a distance from the plasma discharge region.[1] Figure 7.1 shows the effect of remote plasma treatment in comparison with untreated sample and direct plasma treatment.[1]

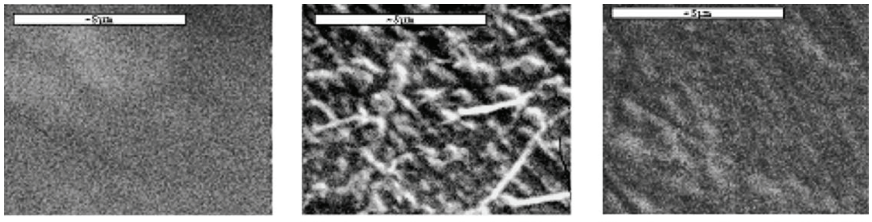

Figure 7.1. SEM of plasma treated PVC film (treatment time 3 min). [Adapted, by permission, from Ru, L.; Jie-rong, C., *Appl. Surface Sci.*, **252**, 14, 5076-5082, 2006.]

The remote argon plasma-treated PVC film surface is similar to the original PVC film. The direct argon plasma-treated PVC film shows a rougher surface. From this comparison it is evident that the remote argon plasma treatment caused lesser changes in surface morphology than the direct argon plasma treatment. There is a limited degradation of surface layers with the remote argon plasma but extensive degradation occurs with direct argon plasma.

Figure 7.2 shows the effect of remote plasma treatment on the contact angle of PVC film. Even very short treatment contributes to very rapid change in contact angle, which

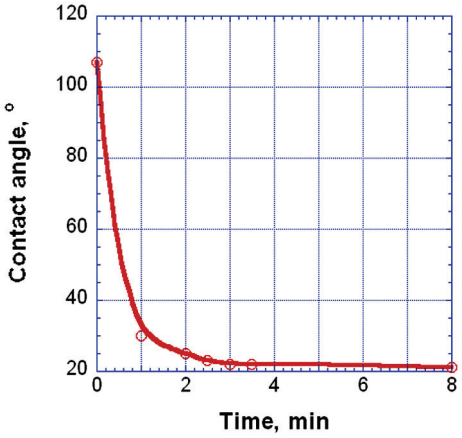

Figure 7.2. Contact angles of PVC films vs. treatment time. [Adapted, by permission, from Ru, L.; Jie-rong, C., *Appl. Surface Sci.*, **252**, 14, 5076-5082, 2006.]

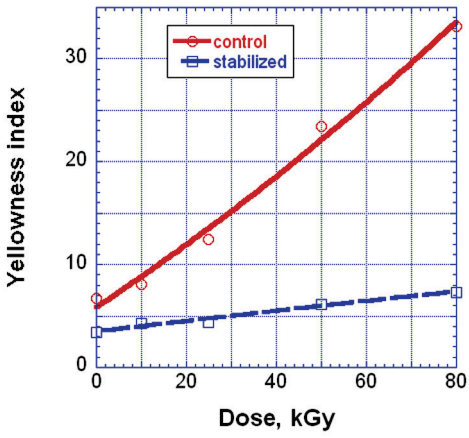

Figure 7.3. Yellowness index of electron beam irradiated samples vs. dose. [Data from Ratnam, C. T.; Zaman, K., *Polym. Deg. Stab.*, **61**, 1, 47-51, 1998.]

then levels off.[1] These changes show that plasma treatment causes a surface to become hydrophillic.

Surface of plasma-treated PVC has a different atomic composition (O/C: control – 0.06; remote plasma – 0.18, and direct plasma – 0.15). The ratio of Cl/C is also changed (control – 0.14, remote plasma – 0.01, and direct plasma – 0.03).[1] Plasma treatment produces a high concentration of carbonyl groups. Extensive dehydrochlorination occurs on the surface and its extent is controlled by the type (direct vs. remote), conditions (energy), and time of treatment.[1]

7.2 β-RADIATION (ELECTRON BEAM)

Radiosterilization methods include β-irradiation in which the energy does not exceed 10 MeV.[2,3] It is important to know changes in PVC not only for the sake of its performance but also because complex formulations of PVC are used for production of materials. Additives used may, on one hand, prevent PVC degradation but also may degrade, producing unwanted chemical components which may be transferred to pharmaceutical, alimentary, or cosmetic products.[2] Analysis of irradiated samples shows the presence of dehydrochlorination, crosslinking, and chain scission.[2] M_n was slightly reduced (5%) which suggests operation of chain scission processes. This is even more visible from polydispersity which was increased by 32%. M_w and M_z were increased by 26 and 50% respectively, which suggests the presence of crosslinking.[2] Exposure to β-radiation in the presence of air (atmospheric oxygen) during sterilization increases dehydrochlorination rate.[3] The operating conditions of sterilization were found to be safe, noninjurious, and reliable.[3]

A direct proof has been presented that dehydrochlorination occurs during electron beam exposure.[4,5] Mass spectra of residual gas were monitored. When a sample is exposed to the electron beam, the atomic masses of 35, 37, 38, and 39 are detected which are chlo-

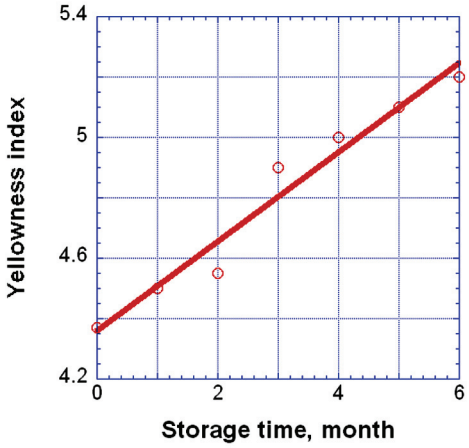

Figure 7.4. Yellowness index vs. storage time. [Data from Ratnam, C. T.; Zaman, K., *Polym. Deg. Stab.*, **61**, 1, 47-51, 1998.]

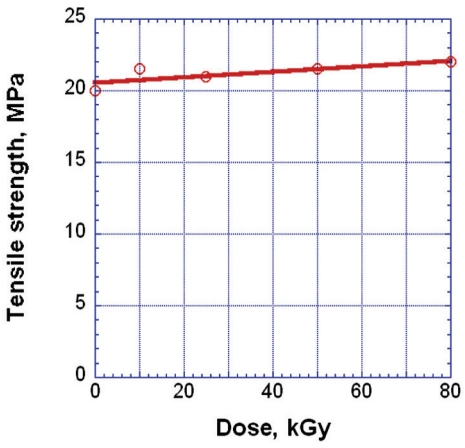

Figure 7.5. Tensile strength vs. dose. [Data from Ratnam, C. T.; Zaman, K., *Polym. Deg. Stab.*, **61**, 1, 47-51, 1998.]

rine and HCl. As soon as the beam is switched off, emission is not detected.[4] Semi-quantitative analysis of the surface by Auger spectroscopy shows that the surface contains 95% C and 5% Cl, which means that there is a chlorine deficiency due to dehydrochlorination.[4,6] Electron beam irradiation promotes ionization and loss of Cl^-.[6]

Figure 7.3 shows that the dehydrochlorination process leads to color change similar to thermal, UV, or γ-degradation.[7] Figure 7.3 also shows that PVC formulations can be stabilized. If PVC is exposed with no thermal stabilizer, yellowness index increases very rapidly. If stabilizers are added, color change is minimal. The stabilized sample contains Ca/Zn thermal stabilizer, epoxidized soybean oil, and UV absorber. Yellowness index changes very little (less than 1 unit of yellowness index during 6 months of storage) for the stabilized sample during storage (Figure 7.4). Figure 7.5 shows that the stabilization effectively prevents tensile strength changes on prolonged exposure (tensile strength is almost constant for the range of exposures).[7]

PVC vulnerability towards electron beam exposure is well known from analytical chemistry.[8,9] During XPS[8] and SEM[9] studies PVC samples degrade and this process has to be minimized by selection of milder conditions and special treatment to obtain meaningful results.

Irradiation of bi-oriented PVC with β-particles (doses from 25 to 100 kGy) causes decrease in yield stress with increased dose of radiation.[10]

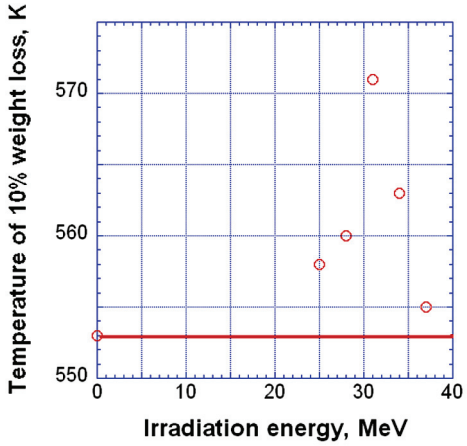

Figure 7.6. Temperature of 10% weight loss in TGA study for samples exposed to different irradiation energy of ion beam. [Data from Senna, M. M.; Abdel-Hamid, H. M.; Hussein, M. A., *Nuclear Instruments Methods Phys. Res. B*, **187**, 48-56, 2002.]

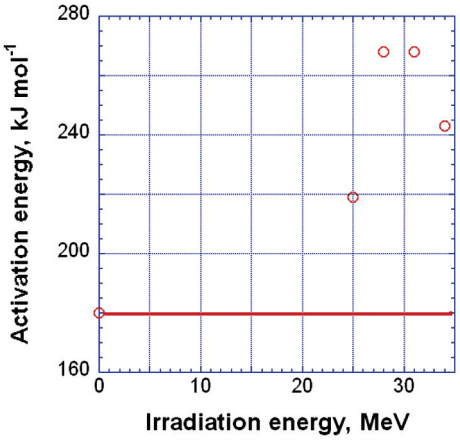

Figure 7.7. Activation energy of dehydrochlorination of samples exposed to different irradiation energy of ion beam. [Data from Senna, M. M.; Abdel-Hamid, H. M.; Hussein, M. A., *Nuclear Instruments Methods Phys. Res. B*, **187**, 48-56, 2002.]

7.3 CORONA DISCHARGE

Corona discharge treatment is commonly used to improve the wettability, adhesion, and biocompatibility of a polymeric surface, without affecting the bulk properties. PVC treatment by corona discharge in helium modifies surface characteristics such as morphology, wettability, functionalization, bonding, and interfacial adhesion and helps to achieve a range of these properties required for medical applications.[11]

PVC containing DOP was treated with a corona discharge beam produced by an electric generator having power of 40 W, 1300 Hz frequency, and 10 kV amplitude for 10 s or 1 min.[11] Only 5 nm thick surface layer was modified. Hydroxyl groups were formed on the surface as a result of oxidation by air which entrained the beam formed by helium-air mixture. Presence of OH groups radically improved surface wettability which is essential for biocompatibility of PVC.[11]

The decolorization of monocomponent basic dyes (Basic Orange, Methylene Blue) was complete in 21 min, whereas 90% bleaching was achieved for acid dyes (Methyl Orange, Eosin Yellowish).[11]

7.4 ION (PROTON) BEAM

Ion beam irradiation was performed using the 40 MeV cyclotron with a scanning system. Samples were irradiated at a constant fluence of 2.25×10^9 ions cm^{-2} with varying energies (25–37 MeV) and at a constant energy (25 MeV) with varying fluence from 2.25×10^9 to 1.0×10^{15} ions cm^{-2}.[13] Figure 7.6 shows that samples are thermally more stable after irradiation than unirradiated control. Figure 7.7 shows activation energy of the first stage of decomposition (dehydrochlorination). Activation energy is substantially higher for irradi-

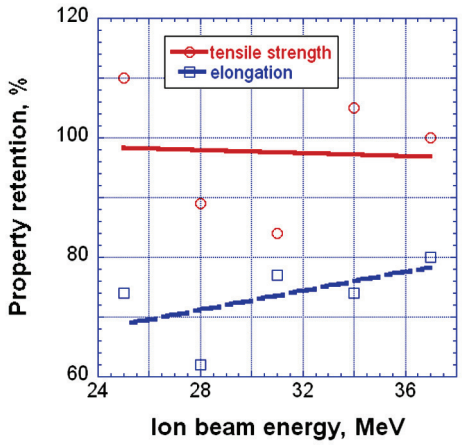

Figure 7.8. Retention of tensile strength and elongation vs. ion beam energy. [Data from Senna, M. M.; Abdel-Hamid, H. M.; Hussein, M. A., *Nuclear Instruments Methods Phys. Res. B*, **187**, 48-56, 2002.]

ated samples than for unirradiated control. This again shows that PVC has higher thermal resistance after irradiation.[13]

Figure 7.8 shows that tensile strength and elongation are very unstable, which suggests that changes occur on the surface and affect measurement error. Tensile strength is much less affected than elongation and the character of changes indicates that both crosslinking and chain scission occur.[13]

In another study, the proton beam of energy between 250 and 750 keV was obtained from a 700 kV van de Graaff accelerator.[14] Using an x-ray detector, Cl loss was monitored during exposure. It was found that, unlike in the above study when two different stages of degradation were observed, in these studies three stages can be distinguished having different reactions to increased dose. In the first stage, Cl loss increases with the highest rate with dose increasing. In the second and the third stages, Cl loss becomes increasingly less dependent on further increase of dose. Only the first stage is identified and it is believed to be dehydrochlorination. The reasons for kinetical changes in the other two stages cannot be explained.[14]

A review reveals that ion beam offers a most valuable tool for altering physical, chemical, structural, surface and interface properties of polymers (including PVC) in a controlled manner and tailoring new materials for basic and applied research for science and technology.[15]

Low energy ion bombardment of PVC samples caused the proportion of chlorine to decrease and oxygen to increase.[16] The wettability and surface energy increased after the treatment.[16] The uniform PVC surface was transformed into a columnar structure containing randomly distributed sharp pillars.[16]

7.5 LASER

Laser radiation has been studied for two purposes: development of knowledge on thermal degradation processes and deposition of various substances on the surface of polymer film.[17-22] The wavelength of radiation can be selected but it is usually chosen to be 193 or 248 nm. These are totally artificial wavelengths which have nothing to do with sun radiation; that is why laser studies cannot be related to weathering but may be useful in assessment of material performance in the outer space. In addition to wavelength, a laser has a collimated, high energy beam which has the ability to instantaneously change the sample temperature which is unusual in comparison with other sources of radiation.

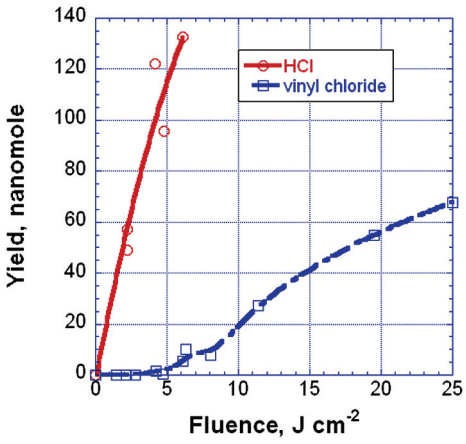

Figure 7.9. Yields of hydrogen chloride and vinyl chloride vs. fluence of CO_2 laser. [Data from Blazevska-Gilev, J.; Kupcik, J.; Subrt, J.; Bastl, Z.; Vorlicek, V.; Galikova, A.; Spaseska, D.; Pola, J., *Polym. Deg. Stab.*, **91**, 2, 213-220, 2005.]

The pulsed CO_2 laser irradiation of PVC leads to ablation of the PVC target and formation of volatile products, such as acetylene, benzene, carbon oxides, hydrogen chloride, methane, vinyl chloride.[19] Figure 7.9 shows the evolution of hydrogen chloride and vinyl chloride vs. fluence. The relative yield of these two major products rapidly increases with fluence. The laser ablative decomposition of PVC reveals two significant differences between the laser-induced and conventional decomposition of PVC: the formation of vinyl chloride and the deposition of the solid polyhydrocarbon with a low Cl content and some degree of unsaturation.[19] The mechanism of degradation is similar to thermal degradation in one essential aspect which is dehydrochlorination with extension of conjugated double bonds. It differs because of cleavage of C–C bonds which results in production of vinyl chloride which is not the case of PVC pyrolytic processes. In addition, the formation of benzene (and toluene) was observed in conventional pyrolysis and ascribed to the degradation of polyenes. Acetylene is likely produced from hot molecules of vinyl chloride and molecular hydrogen is formed by C–H cleavages and H atom abstraction reactions.[19]

PVC film has high attenuation ($\mu \sim 7.5$ mm^{-1}) at 240 nm which decreases rapidly to a constant level for wavelengths longer than approximately 330 nm. At 240 nm the maximum thickness of film which obtains constant radiation within the error of 10% is about 0.1 mm, whereas above 330 nm this limit will be extended to film thickness of about 1.8 mm.[18] These data illustrate very well the penetration depth of different wavelengths. Radiation below 240 nm is completely absorbed on the surface. That is why it is customary to use a laser having radiation of 248 nm for limited penetration studies and laser with wavelength of 193 nm for surface erosion studies.

From the fundamental point of view, the pulsed UV laser treatment of a polymer introduces two different mechanisms: a photothermal energy conversion dominant at long wavelength ($\lambda = 308$ nm) or a direct photochemical process at shorter wavelengths such as $\lambda = 193$ or 248 nm. In the photothermal process the photon energy is transformed into lattice vibrations (phonons), either directly or by de-excitation from any laser induced excited state, whether electronic, excitonic, or other.[20] Most polymers have a high absorption coefficient and they may be etched by wavelength $\lambda = 193$ nm because the corresponding photon energy is about 6.4 eV and thus larger than any polymer bond strength.[20] At very high fluence, PVC is left with a fresh, ablated surface.[20] There is a certain fluence threshold of 50 mJ cm^{-2}. Below this threshold value, the dehydrochlorination process is

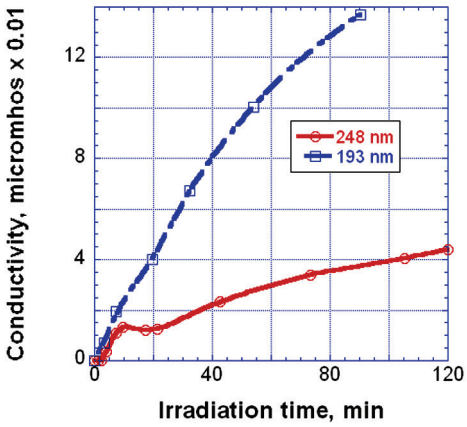

Figure 7.10. Conductivity of HCl solution vs. irradiation time by lasers having two different wavelengths. [Data from Sheu, L.; Imen, K.; Allen, S. D., *J. Appl. Polym. Sci.,* **77**, 1, 59-63, 2000.]

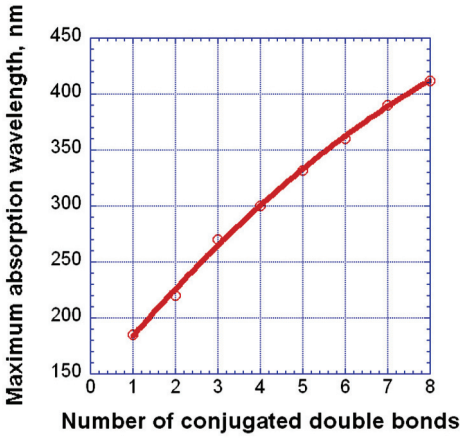

Figure 7.11. Maximum absorption wavelength of polyenes of different length. [Data from Sheu, L.; Imen, K.; Allen, S. D., *J. Appl. Polym. Sci.,* **77**, 1, 59-63, 2000.]

dominant, above the threshold value, ablative photodecomposition processes occur. A clean surface is obtained above 400 m cm^{-2}.[20]

Figure 7.10 shows that radiation of 193 nm produces higher dehydrochlorination rate which can be predicted from their fluences (193 nm – 7.37 mJ cm^{-2} and 248 nm – 6.59 mJ cm^{-2}).[22] Figure 7.11 shows the absorption maxima of polyenes having various length.[22] It was discovered that the longer wavelength of radiation (248 nm) tends to produce longer polyenes.[22]

Ethyl-N-phenylmaleimide-4-carboxylate was found to be an effective stabilizer protecting PVC against laser radiation (effective concentration is 10 mmol of stabilizer per 100 g PVC).[17,21] The stabilized polymer is almost undamaged by laser pulses of up to 8.5 J cm^{-2}.[17]

Microdrilling conditions by laser, such as wavelength, fluence, and frequency were investigated.[23] This is important for limiting aspect ratio, circularity and heat affected zone during drilling holes in the material.[23]

7.6 METALLIZATION

Polymer metallization can be carried out by physical vapor deposition, thermal evaporation, ion beam or magnetron sputtering, and chemical vapor deposition.[24] Metallized polymers play an important role in the microelectronics industry in thin-film transistors and compact discs. Metallization of PVC could in principle remove the need for photostabilization by providing a conductive and photoimpermeable barrier.[24]

Physical vapor deposition of Fe, Ni, Cu, Ag, and Au on PVC has been studied.[24] At low metal exposures, metals reacted with PVC, forming metal chlorides. For metals with more than one stable oxidation state, the salt produced corresponded to the metal's lowest

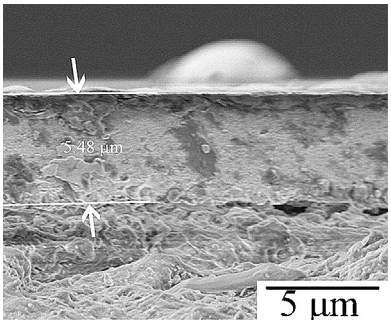

Figure 7.12. Nickel plating on PVC surface. [Adapted, by permission, from Wang, M.-Q.; Yan, J.; Du, S.-G.; Li, H.-G.; Appl. Surf. Sci., 277, 249-56, 2013.]

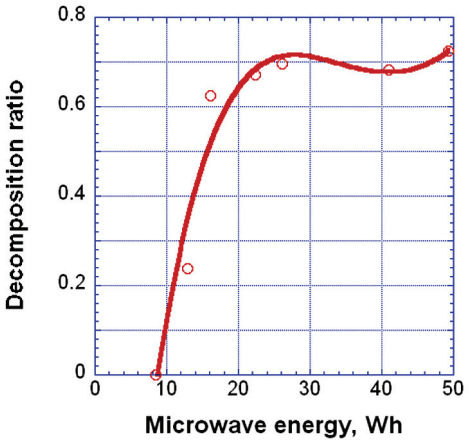

Figure 7.13. Decomposition ratio (absorbed microwave energy/decomposition yield) vs. microwave energy. [Data from Moriwaki, S.; Machida, M.; Tatsumoto, H; Otsubo, Y.; Aikawa, M.; Ogura, T., *Appl. Thermal Eng*., **26**, 7, 745-750, 2006.]

stable oxidation state (e.g., CuCl instead of $CuCl_2$). Higher metal exposures resulted in deposition of a metallic overlayer.[24]

The deposition efficiency of copper on PVC surface is highly sensitive to the glass transition temperature of the substrate, irrespective of the process gas pressure.[25] The electrical conductivity of the coating is fairly low due to the pores and inter-particle defects.[25]

A semi-interpenetrating polymer network made out hydrogel film was applied to modify the poly(vinyl chloride) surface before electroless plating with nickel.[26] The hydrogel layer was used as the chemisorption site for nickel ions.[26] SEM and XRD show that a compact and continuous Ni–P layer with amorphous nickel phase formed on the PVC surface.[26] Figure 7.12 shows that metal layer forms a continuous layer on the PVC surface without voids and interlaminar delamination.[26]

7.7 MICROWAVE

Microwave radiation is widely used in the home appliance and industry, therefore it is of interest to learn about its effect on PVC decomposition.[27,28] The efficiency of dielectric heating increases at temperatures above the glass transition temperature.[27] Figure 7.13 shows that there is a threshold of energy (about 10 Wh) below which degradation does not occur. Above this threshold value, degradation yield rapidly increases with energy increasing until the degradation yield levels off.[28] Dehydrochlorination is the main mechanism of degradation. Addition of components of formulation which absorb microwave energy, such as carbon black or Zn-Mn ferrite, drastically increases degradation rate.[28] Figure 7.14 shows that the increased temperature at which microwave degradation occurs increases the degradation rate.[27]

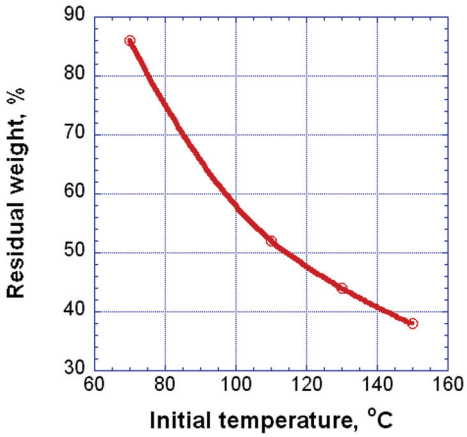

Figure 7.14. Residual weight vs. initial temperature. [Data from Ito, M.; Ushida, K.; Nakao, N.; Kikuchi, N.; Nozaki, R.; Asai, K.; Washio, M., *Polym. Deg. Stab*., **91**, 8, 1694-1700, 2006.]

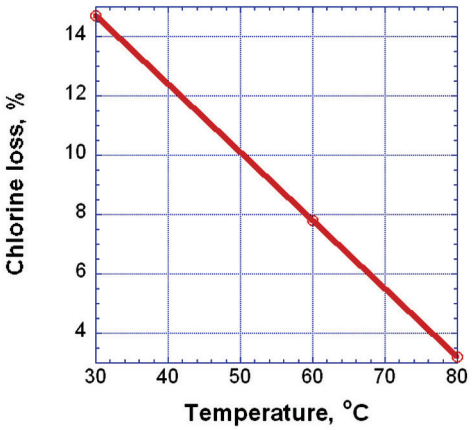

Figure 7.15. Chlorine loss vs. temperature of neutron irradiation. [Data from Reddy, S. J.; Mauerhofer, E.; Woehr, A.; Denschlag, H. O., J. Radioanal. Nuclear Chem., 223, 233-234, 1997.]

7.8 NEUTRON IRRADIATION

Unexpected results were obtained in unusual studies. Small PVC samples were placed in sulfuric acid in sealed vials and exposed to neutron radiation at different temperatures.[28] Figure 7.15 shows that the higher the exposure temperature, the lower the loss of chlorine (the lower the degradation rate). If samples were exposed to heat and sulfuric acid, no chlorine loss was detected.[29] It was noticeable that the structure of PVC films depended on temperature. Irradiation at 30°C did not change the structure; at 60°C sample partially shrunk, and at 80°C the sample completely shrank and became hard.[29] This finding suggests that chlorine loss depends on the structure (morphology) of polymer, as, for example, formation of a stable polyene (e.g., similar to *cis/trans* isomers in explanation of the mechanism of propagation and termination in thermal degradation).[29]

7.9 OXYGEN PLASMA

Microwave discharge is used to produce oxygen plasma useful in improvement of surface properties of polymers.[30] Oxygen plasma has also been used as a rapid weathering test.[31]

Figure 7.16 shows an SEM micrograph with a characteristic surface of PVC treated with oxygen plasma.[30] The surface is clearly inhomogeneous because of the etching process. In order to understand chemical changes, several spectroscopic methods and XPS were used. Data indicate that the mechanism of changes should include two stages: dehydrochlorination and dehydrogenation. Data also show extensive oxidation which leads to

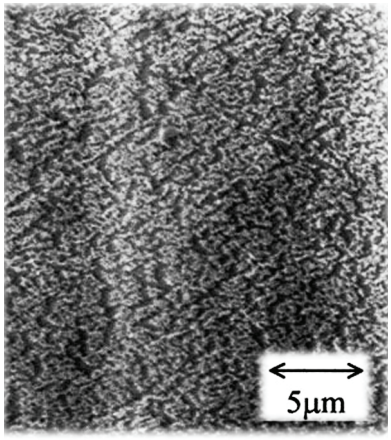

Figure 7.16. SEM micrograph of PVC treated with oxygen plasma. [Adapted, by permission, from Kumagai, H.; Tashiro, T.; Kobayashi, T., *J. Appl. Polym. Sci.*, **96**, 2, 589-594, 2005.]

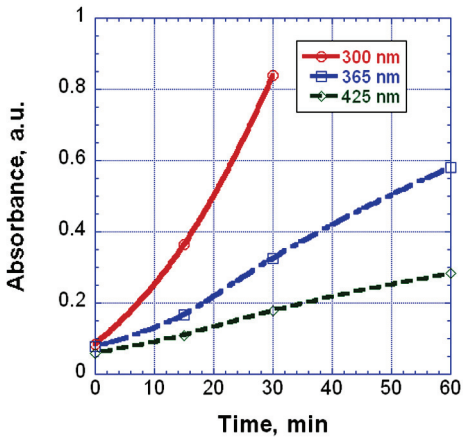

Figure 7.17. Absorbance of UV/visible radiation vs. time of exposure to x-rays. [Data from Sbampato, M. E.; Kawano, Y., *Eur. Polym. J.*, **21**, 10, 909-914, 1985.]

formation of carbonyl groups. The following reactions characterize the main reaction pathways:

$$\sim\!(CH_2CHCl)_n\!\sim \xrightarrow[-H_2\ -Cl]{\text{plasma}} \sim\!(CH{=}CH)_n\!\sim \xrightarrow[-2H]{\text{plasma}} \sim\!(C{\div}C)_n\!\sim$$

The oxygen plasma has been applied to a window profile made out of PVC. In order to find a rapid test of their durability on exposure to atmospheric conditions. The results were compared with data derived from extensive artificial and natural weathering of these materials. The plasma erosion technique caused a very rapid loss of gloss but had a comparatively small impact on microhardness and color. The results showed no correlation with the data derived from the weathering studies.[31]

Compared with direct-oxygen-plasma sterilization, remote plasma sterilization enhances the hydrophilic properties and limits the degradation of the PVC surface.[32] PVC surface energy is increased more than twice.[32] Remote-plasma sterilization increases oxygenated functional groups on PVC surface.[32] Remote plasma inactivates *Escherichia coli* on medical PVC products and helps to optimize their surface properties.[32]

7.10 X-RAYS

The x-ray degradation of PVC films has been investigated by both IR and UV/visible absorption spectroscopies. Figure 7.17 shows absorption of UV/visible light at three wavelengths.[33] The wavelengths selected are equivalent to absorption by polyenes having length of 4, 6, and 8 double bonds. It is pertinent from this data that dehydrochlorination is dominant (especially since irradiation occurred in a vacuum).[33] Dehydrochlorination is the major mechanism of degradation by x-rays.[34] The transparent films become slightly yel-

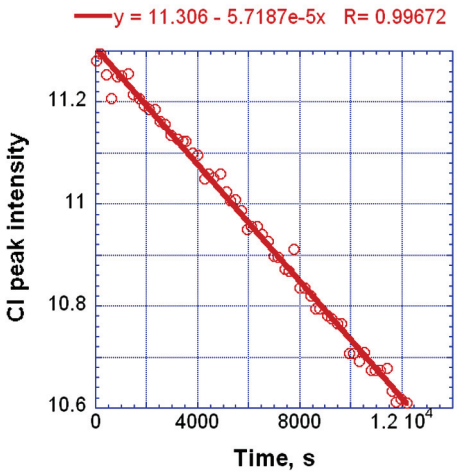

Figure 7.18. Cl peak intensity vs. x-ray exposure time of PVC sample. [Adapted, by permission, from Yoshihara, K.; Tanaka, A., *Surface Interface Anal.*, **33**, 252-258, 2002.]

low during irradiation.[33] If irradiated samples were stored in air, they developed new peaks relative to carbonyl groups which is caused by reaction of radicals with atmospheric oxygen.[33]

Most studies on the effect of x-ray radiation on PVC were conducted to estimate the effect of XPS analysis on analyzed samples[8,35,36] XPS uses soft x-ray radiation. Interlaboratory study was conducted to establish the effect of x-rays used in XPS on PVC.[35] It was concluded that the rate constant of the degradation for PVC can be obtained from the peak intensity changes of Cl 2p photoelectrons assuming first-order reaction with photons.[35] Figure 7.18 shows that there is an excellent correlation between PVC dehydrochlorination and time of exposure.[35] In the follow up studies, various x-ray sources have been studied and they had comparable effects on the degradation rate.[8] Measurements as a function of angle of emission show that the loss of Cl is mainly confined to the outermost layer of 5.8 nm from the surface.[8] The spectrometers measuring the spectrum at 60° emission angle measure a higher rate constant than those for normal emission.[8] It was established that to minimize the influence of x-ray radiation studies of PVC using XPS surface analysis, a complete analysis of a polymer sample should not take more than 10 min of x-ray exposure in order to avoid notable polymer degradation.[36]

7.11 ULTRASONIC

Intensive ultrasonic irradiation of liquids causes cavitations which generate excited species such as radicals at relatively high concentrations. The radicals may then initiate chemical reactions on the surface of immersed polymer.[37] An additional effect occurs near a solid surface where cavitational collapse is asymmetric and a microjet of liquid containing radicals impinges at high speed on the solid.[37] Therefore, solid particles influence sonochemical reactions.[37] Several liquid media were studied including water, ethylene glycol, glycerine and Fluorinert. All liquids were suitable for the purpose but Fluorinert gave maximum cavitation intensity and thus the dehydrochlorination rate.[37] It was concluded that sonochemical dehydrochlorination can be applied to modify PVC surface.[37]

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8

Mechanodegradation

Mechanochemical degradation occurs during processing and use of PVC products. Most processing methods require elevated temperature which also influences degradation of PVC materials. It is therefore very difficult to separate both influences. Some fundamental studies use various methods of milling and grinding to study mechanical degradation, in which case the results are least affected by temperature.

Below, we discuss the following methods of mechanodegradation:

- extrusion,[1,2]
- injection molding,[2,3]
- milling and grinding,[4-8]
- PVC mixing with additives,[9]
- Brabender plastograph mixing,[10]
- capillary and torque rheometry,[11-13]
- processed materials.[14-16]

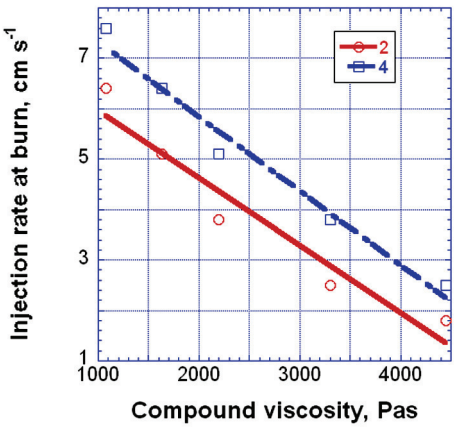

Figure 8.1. Injection rate at burn vs. viscosity of PVC compound processed by injection molding using 2 pin gates and 4 tab gates. [Data from Summers, J. W.; Toyoda, P.; Weir, S.; Beal, C.; Toensing, C., *J. Vinyl Additive Technol.*, **2**, 2, 129-133, 1996.]

Repeated extrusion is frequently used to estimate the effect of processing on a particular formulation.[1] This type of study offers data important for practical purposes (e.g., potential usefulness of regrind recycling) but data cannot be used directly for estimation of the influence of mechanochemical degradation because both thermal treatment and mechanical energy are applied and their influence cannot be separated. In repeated extrusion,[1] color, gloss, tensile strength, and molecular weight almost did not change during five extrusion cycles, and estimated lifetime after the last extrusion was still 47 years, which indicates that the mixture was very well stabilized.[1]

Figure 8.1 shows data for injection molding which indicate that if more obstacles are created with the same viscosity of compound and injection speed, burning of the compound will more likely occur. This data does not give a chance to separate influences of temperature and shear but it illustrates correctly that increased shear may cause rapid degradation because of compound over-

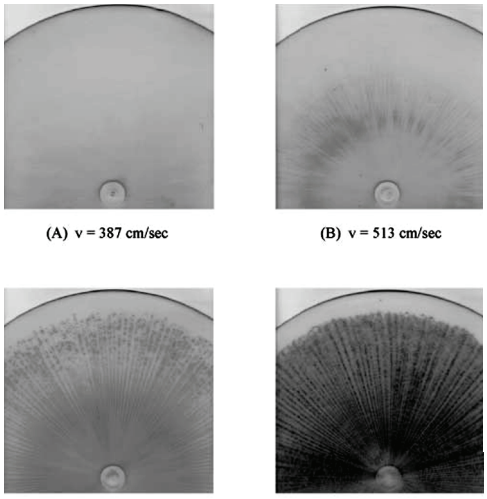

Figure 8.2. Burning in radial mold (temperature = 200°C) vs. injection velocity as marked. [Adapted, by permission, from Garcia, J. L.; Koelling, K. W.; Xu, G.; Summers, J. W., *J. Vinyl Additive Techno*l., **10**, 1, 17-40, 2004.]

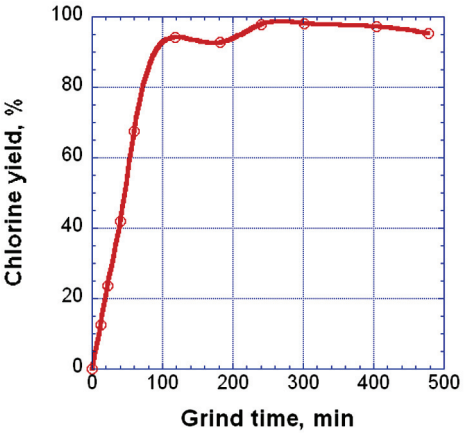

Figure 8.3. Chlorine loss from PVC vs. grind time with CaO. [Data from Tongamp, W.; Zhang, Q.; Saito, F., *J. Hazardous Mater.*, **137**, 2, 1226-1230, 2006.]

heating. Shear heating is influenced by mold design (e.g., number of gates), injection velocity, and compound viscosity which were at play in this example.[2] The photographic example in Figure 8.2 illustrates dramatic changes (burning) caused by gradually increasing injection velocity.[3] The degradation occurs in a radial direction away from the sprue.[3]

The above examples show that mechanical forces cause degradation but the magnitude of this degradation cannot be evaluated because the effect of two influences (temperature and shear) cannot be resolved. Figure 8.3 shows the effect of extensive grinding of PVC with calcium oxide on chlorine loss from PVC.[5] The following reaction occurs during grinding:

$$\sim\!(CH_2\!-\!CHCl)\!\sim + CaO \longrightarrow \sim\!(CH\!=\!CH)\!\sim + CaOHCl$$

Complete decomposition of PVC was achieved with CaO within 2 h of grinding. Under similar experimental conditions, more than 95% of Cl in PVC was removed by $CaCO_3$ and $Ca(OH)_2$ in 4 and 12 h, respectively.[5] Although there is no heat supplied to the mixture during grinding it can be expected that temperature has effect on HCl loss but the source of the energy is mechanical.

Molecular weight decrease was observed during mechanochemical degradation by vibromilling for different lengths of time (Figure 8.4).[6] Jet milling produced comparable results in molecular weight reduction.[6] Figure 8.5 shows that crystallinity is also decreased (1435 cm^{-1} and 1427 cm^{-1} are amorphous and crystalline absorption bands, respectively).[6]

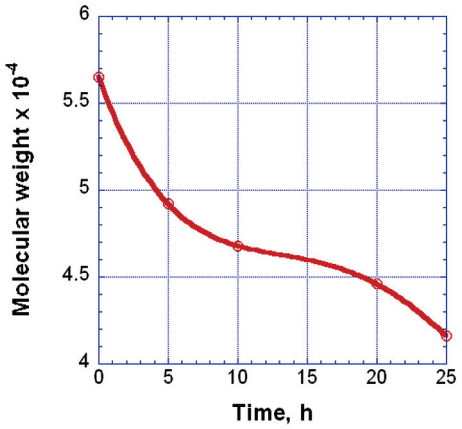

Figure 8.4. Molecular weight of PVC after vibromilling vs. time. [Data from Xu, X.; Guo, S.; Wang, Z., *J. Appl. Polym. Sci*., **64**, 12, 2273-2281, 1997.]

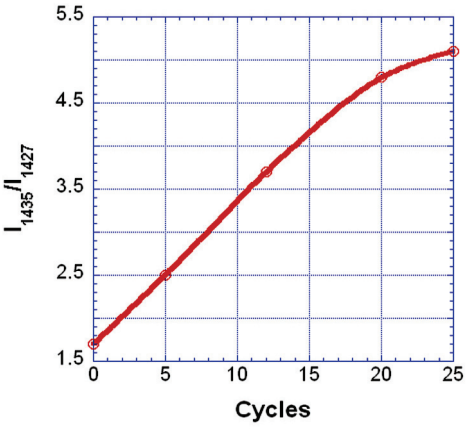

Figure 8.5. Crystallinity vs. jet milling time. [Data from Xu, X.; Guo, S.; Wang, Z., *J. Appl. Polym. Sci*., **64**, 12, 2273-2281, 1997.]

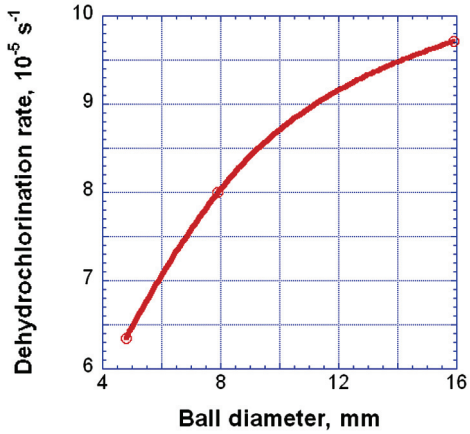

Figure 8.6. Dehydrochlorination rate during PVC grinding with CaO in ball mill vs. ball diameter. [Data from Mio, H.; Saeki, S.; Kano, J.; Saito, F., *Environ. Sci. Technol.*, **36**, 1344-1348, 2002.]

Figure 8.6 shows that the dehydrochlorination rate increases with increasing ball diameter.[7] Larger balls give higher impact energy, which results in increased degradation.

Composition of inorganic material used for grinding with PVC has an effect.[8] The so-called blast furnace slag, which is a mixture of CaO and SiO_2 was found to be the most effective dehydrochlorinating additive and $CaCO_3$ was the least effective additive.[8] In a planetary ball mill, complete dehydrochlorination of PVC was achieved during 4 h. CaO in the slag mixture plays the role of a reactive additive which reacts with HCl, whereas SiO_2 is a grinding aid which facilitates mechanochemical degradation.[8] Vibromilling was also very effective in increasing interaction between PVC and nano-SiO_2.[9] This was similar to vibromilling of PVC and $CaCO_3$ in the presence of a coupling agent which improved properties of the composite.[4]

A Brabender mixer is frequently used to determine formulation stability. Figure 8.7 shows typical Brabender data of torque vs. time of mixing. Rapid increase in torque marks extensive degradative processes. Similar to previously described studies on extrusion and

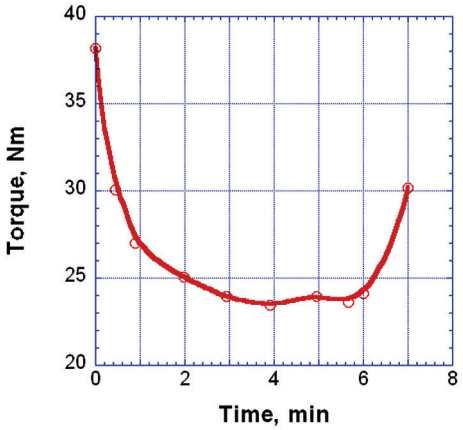

Figure 8.7. Brabender mixer output for PVC mixed at 190°C at 60 rpm. [Data from Wenguang, M.; La Mantia, F. P., *J. Appl. Polym. Sci.*, **59**, 5, 759-67, 1996.]

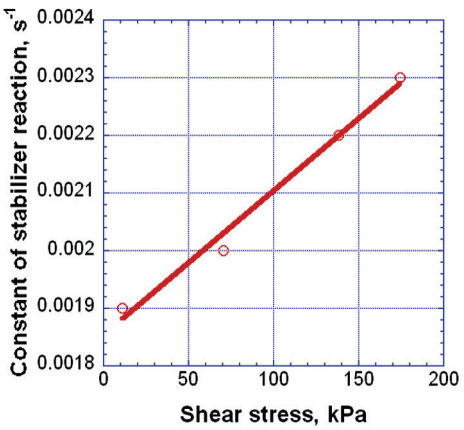

Figure 8.8. Rate constant of Ca/Zn stabilizer reaction vs. shear stress. [Data from Bacaloglu, R.; Fisch, M.; Steven, U.; Bacaloglu, I.; Krainer, E., *J. Vinyl Additive Technol.*, **8**, 3, 180-193, 2002.]

injection molding, these data also do not allow us to separate the effect of temperature and shear energy on degradation which give a cumulative response.[10]

Capillary rheometry can also be used to estimate the effect of shear rate (Figure 8.8), although again, temperature together with mechanical shear are essential factors controlling the degradation rate of PVC and thus stabilizer reaction rate.[11]

Torque rheometry is frequently used for various purposes, including estimation of the influence of mechanodegradative forces.[12-14] Radical processes and the effect of nitroxyl radicals on PVC stabilization were investigated by torque rheometry.[12,13]Oxidation of the hindered amines occurs very rapidly and completely during mechanooxidation.[12]

Solid materials under stress are also subjected to mechanodegradation processes. Zhurkov *et a1*.[17] have estimated that for each microcrack, there are on the average 1000 stable ends in solid polymer under stress. Once a solid polymer is stressed, mechanical degradation could be initiated due to the formation of mechanoradicals. When a PVC film is subjected to mechanical creep, mechano-radicals are formed by chain scission. Two radicals formed abstract hydrogen, which begins a chain of propagating reactions. The effect of stress on the thermal degradation rates of polymers can be fitted to an empirical Arrhenius-like equation that is attributed to Zhurkov:

$$\phi = A\exp\left[-\frac{(\Delta G - B\sigma)}{RT}\right] \qquad [8.1]$$

where:

A,B	constants,
ΔG	"apparent" activation energy,
σ	stress,
T	absolute temperature,
R	gas constant.

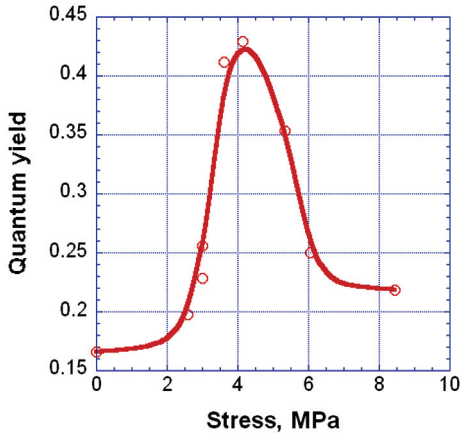

Figure 8.9. Quantum yield vs. tensile stress. [Adapted, by permission, from Chen, R.; Tyler, D. R., *Macromolecules*, **37**, 5430-5436, 2004.]

Figure 8.9 shows the effect of tensile stress on quantum yield of PVC degradation. These results support the decreased radical recombination efficiency, DRRE hypothesis, one of several hypotheses that have been proposed in the literature to explain the effect of stress on polymer photodegradation rates and efficiencies.[16] The DRRE hypothesis proposes that the function of stress is to increase the initial separation of the photochemically generated radical pair, which has the effect of decreasing their recombination efficiency and thus increasing degradation efficiency.[16] The hypothesis predicts an eventual downturn in degradation efficiency because of polymer chain ordering; the increased order hinders diffusion apart of the radicals and thus increases their probability of recombination.[16]

The wear resistance is also affected by mechanochemical degradation. The addition of various fillers to PVC matrix modifies the wear-resistance of the composites. Silica fillers and wollastonite show the highest improvement in the wear resistance, most likely because of interaction with PVC.[15]

The mechano radicals and mechano anions of polypropylene, polyethylene, poly(vinyl chloride), poly(vinyl fluoride), poly(vinylidene fluoride), polytetrafluoroethylene, and bacterial cellulose were detected.[18] Ionic yields of various polymers are as follows: PE – 0.11, PTFE – 0.17, PP – 0.36, PVC – 50, PVF – 0.66, and PVDF – 0.78.[18] This shows that PVC is vulnerable to mechanodegradation.[18]

The contact electrification is caused by the electron transfer from the donors to the acceptors during contacting on the friction surface.[19] The donors are mechano anions and mechano radicals, and the acceptors are mechano cations and mechano radicals.[19] Net charge on polymer depends on its position in the triboelectric series, and it polymers can be ranked as follows from positive, PP < PE < PVC < PVF ~ PVDF < BC < PTFE to negative.[19] Tribochemical effect influenced polymer degradation.[20]

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9

Chemical Degradation

After the first studies on chemical dehydrochlorination had been published,[1] no further interest was shown in that field for about 20 years. At the beginning of the 1960's some work was initiated on chemical dehydrochlorination in order to obtain semi-conductive polymers that eventually could be used in modern electronics.[2-4] Studies in that field have been partially given up as new possibilities were shown to be more attractive, e.g., polyacetylene synthesis, compounds containing metal ligands that can form one-dimensional polymers with a metal core, and numerous conductive polymers which are being explored. Now, the field of application of these studies shifted to the methods of recycling and recovery[5-7] and applications for analytical purposes.[8]

There are several more theoretical areas in which studies on the chemical dehydrochlorination of PVC are continued, such as kinetics of reaction;[9-18] comparison of thermal and chemical dehydrochlorination;[19,20] changes in PVC physical properties after chemical, thermal and photochemical degradation;[21] and correlation of alkaline dehydrochlorination kinetics with the length of polyenes formed.[19,20]

Some other issues are also connected with these studies, such as preparation of material for analysis of the physical behavior of semiflexible polymer in solution in order to determine the structure of a polymer chain. Other work done on the interaction of chemically dehydrochlorinated polymer and trifluoroacetic acid was aimed at studying the possibility of the migration of double bonds along the polymer chain.[22,23] Additional work has been done on the preparation of raw material for further chemical modification[24] and chlorination[25] or block copolymer synthesis.[26] A good deal of interest has been devoted to the so-called photobleaching reaction[19,20,27-30] in order to understand the mechanism of that reaction, the contribution of polyene sequences on absorption in UV and visible regions, factors limiting color formation in degraded PVC, and measurement methods of concentration of short polyenes present in the initial polymer.

9.1 METHODS OF CHEMICAL DEHYDROCHLORINATION

The procedure of chemical elimination of HCl from the PVC chain developed by Benough[10] and Shindo,[9] after a few modifications, is used. Poly(vinyl chloride) is dissolved or swollen under an oxygen-free atmosphere. Care is always taken that solvents are peroxide-free (purified prior to use) in order to avoid oxidation of the double bond formed in the elimination reaction. After the polymer has been dissolved, the ethanol solution of base is added to initiate reaction. Typical experimental conditions are shown in Table 9.1.[16] The reaction is followed by neutralization with diluted HCl; then the product is left in distilled water for 24 hrs, dried in a vacuum over $P_2 0_5$, and stored under nitrogen in

darkness. Taking into consideration the reaction conditions, one should expect the possibility of interaction of solvent traces left in the sample with PVC molecules[30] and formation of charge transfer complexes with THF,[31] which might influence the results of some studies performed on these materials.

Table 9.1. Reaction conditions for alkaline dehydrochlorination of PVC. [Data from Ref. 16.]

Solvent type	Solvent, ml	PVC, g	Ethanol, ml	KOH, g	Temp., K	Reaction time, min
THF	550	20	50	5	278	300
THF	1200	150	250	26.5	280	–
Dioxan	360	127	75	8	288	–
Dioxan	900	310	150	16	293	480

Reaction with alkoxide was used to obtain polyacetylene-like materials according to the following method.[17,18] All solvents used were distilled, dried, and stored over molecular sieves.[17,18] Tetrahydrofuran was stored under a nitrogen atmosphere and freshly distilled before the use.[17,18] Dehydrochlorination was conducted with and without matrix (product of dehydrochlorination is insoluble, therefore for some studies it is more convenient to conduct studies with dehydrochlorination occurring in a matrix of another polymer).[17,18] Poly(vinyl butyral) was used as a matrix polymer. The alkoxides were prepared immediately before use by dissolving potassium pieces in the corresponding alcohol. All reactions were done in a nitrogen atmosphere at 295 K.[17,18] To dehydrochlorinate PVC without a matrix, a potassium tert.-butoxide or potassium n-butoxide solution (1.31 mmol in 20 ml tert.-butanol or n-butanol, respectively) was added to a PVC solution in THF (1.28 mmol in 200 ml).[17,18] To dehydrochlorinate PVC in the presence of a matrix, 1 g PVB was dissolved in a PVC solution (1.28 mmol in 160 ml THF).[17,18] The reaction was started by the addition of a potassium n-butoxide solution (5.1 mmol in 80 ml n-butanol) or a potassium tert.-butoxide solution (5.1 mmol in 80 ml tert.-butanol).[17,18]

In another study, dehydrochlorination was conducted on material already preformed as a film with polyethylene glycol, PEG, used as a catalyst.[4] The PVC films were cast from tetrahydrofuran solution of PVC (0.04 g ml^{-1}) containing a certain amount of PEG (volume ratio of THF and PEG was 10:1) and then the dry PVC film was treated with aqueous potassium hydroxide KOH solution (40% by weight) at room temperature.[4] The reaction occurred under a nitrogen atmosphere to avoid the possibility of oxidation of dehydrochlorinated polymer.[4] The films were washed three times with large amounts of distilled water and methanol, and then successively extracted in a Soxlet extractor with methanol for 48 h to remove PEG, base, and salt.[4] The clean product was dried under vacuum for 24 h at room temperature.[4]

The so-called reductive dechlorination was used to determine branching characteristics of PVC. Dechlorination with tri-n-butyltin hydride or tri-n-butyltin deuteride was performed by following a two-stage procedure.[32] Azobisisobutyronitrile was used for thermal initiation, and the solvents used in the first and second stages were anhydrous THF and anhydrous m-xylene, respectively.[32] After precipitation into methanol, followed by Soxlet

extraction with methanol and subsequent drying, the reduced polymers required no further treatment before they were analyzed by NMR.[32] Further details can be found elsewhere.[33]

A method was developed for dehydrochlorination of rigid PVC pellets as a method of recovery of valuable contents from PVC.[6] A rigid PVC pellet (0.2 g) and 20 ml of 0-7 M NaOH solutions were put in a 25 ml tube. Several tubes were put in the aluminum block heated to the prescribed temperature and held for the reaction time.[6]

A different method with a similar purpose is used to degrade PVC under high pressure and high temperature in water.[7] Constant temperature and constant pressure were applied for a given time using a supercritical water reaction apparatus.[7] The reaction temperature was kept constant after raising the temperature from room temperature at a heating rate of 5°C/min. The decomposition reaction was monitored by the amount of PVC residue and the content of chlorine determined by a gravimetric method.[7]

In the previous method HCl dissolves in water and solid remainder can be processed without further corrosion and health hazards. The thermochemical method attempts to achieve the same goal by different means.[5] In the reactor, the chlorine from the PVC reacts with fillers producing calcium chloride. The metal stabilizers (lead, cadmium, zinc and/or barium) are converted to metal chlorides. Exploiting the influence of pH, temperature, liquid to solid ratio and different metal solubilities, metals and calcium chloride are sequentially extracted from the reaction product. Figure 9.1 shows the schematic diagram of the process.

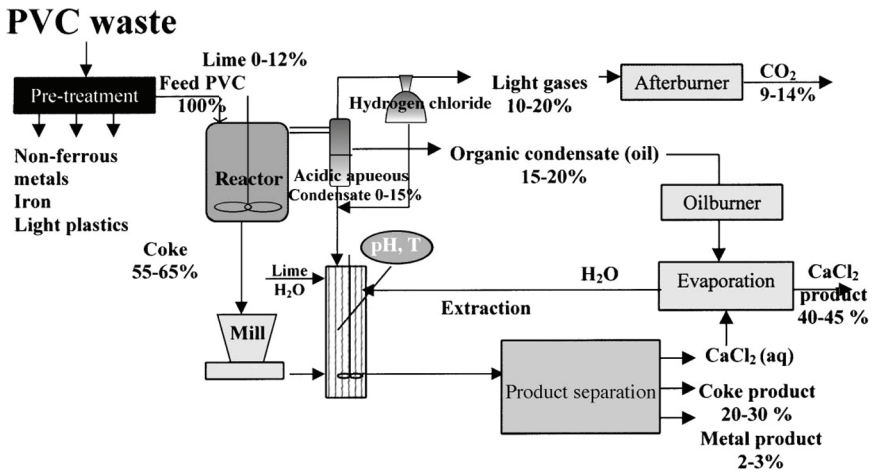

Figure 9.1. Process for treatment of PVC waste. [Adapted, by permission, from Jaksland, C.; Rasmussen, E.; Rohde, T., *Waste Management*, **20**, 463-467, 2000.]

This process is similar in concept to several methods of mechanodegradation of PVC by vibro- and ball milling with different fillers discussed in the previous chapter.

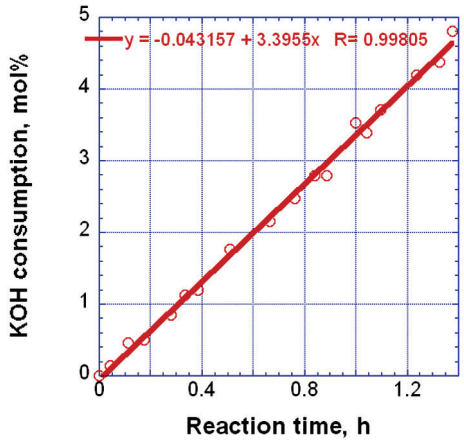

Figure 9.2. The degree of dehydrochlorination versus reaction time. Data from KOH consumption and Cl evolution. [Data from Ostensson, B.; Flodin, P., *J. Macromol. Sci.-Chem.*, **A12**, 249, 1978.]

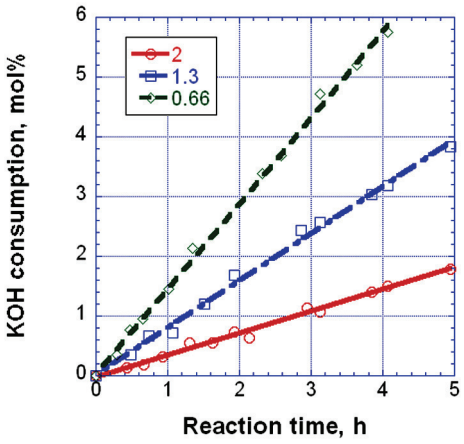

Figure 9.3. KOH conversion at 282.5K vs. reaction time for various PVC/KOH ratios. [Data from Ostensson, B.; Flodin, P., *J. Macromol. Sci.-Chem.*, **A12**, 249, 1978.]

9.2 KINETICS AND MECHANISMS OF REACTION

Reaction kinetics can be studied by titration of the unreacted KOH or KCl produced from reaction, titration of HCl dissolved in water,[7] determination of amount of chlorides,[5] weight loss,[6] chlorine content,[17,18] or UV-visible spectroscopy of polymer. Flodin *et al.*,[15,16] used automatic base-acid titration and mercuric nitrate titration to establish the HCl elimination rate (Figure 9.2).

The reaction rate was constant until 30% KOH was reacted. The reaction followed a pattern of pure HCl elimination, as no hydroxyl group was detected by IR spectroscopy.

The concentration of reagents determines the rate of dehydrochlorination, as illustrated in Figure 9.3. As an increase in concentration of KOH causes a more or less proportional increase in reaction rate, the reaction is a second-order reaction. The same reaction order was proposed by Shindo,[11,12] who has shown the process of HCl alkaline elimination as a chain of consecutive reactions as follows:

$$\mathrm{KOH + PVC \xrightarrow{k_1} P_1 + KCl + H_2O}$$
$$\mathrm{KOH + P_1 \xrightarrow{k_2} P_2 + KCl + H_2O}$$
$$\vdots$$
$$\mathrm{KOH + P_{n-1} \xrightarrow{k_n} P_n + KCl + H_2O}$$

Their rates form a set of differential equations:

$$d[P_1]/dt = k_1[KOH][PVC] - k_2[KOH][P_1]$$
$$d[P_2]/dt = k_2[KOH][P_1] - k_3[KOH][P_2]$$
$$.$$
$$.$$
$$.$$
$$d[P_n]/dt = k_n[KOH][P_n]$$

Flodin *et al.*[15,16] assumed that concentrations of partially reacted products are small when compared with PVC concentration and arrived at a general equation, as follows:

$$d[E]/dt = k_1[KOH][PVC]$$

where:

[E] the total concentration of double bonds in all polyene sequences.

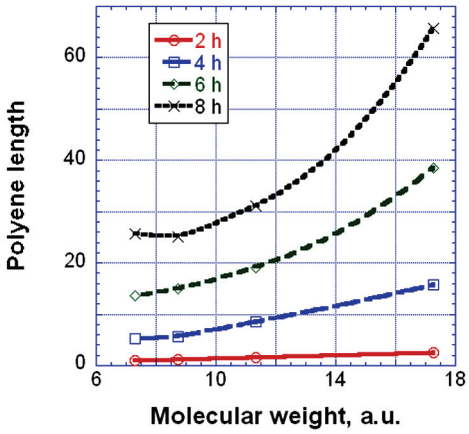

Figure 9.4. Molecular weight vs. the total number of conjugated double bonds in polyene sequences in a dehydrochlorinated PVC chain at various reaction times as labeled. [Data from Shindo, Y., *J. Polym. Sci. Polym. Letters Ed.*, **10**, 555, 1972.]

Based on this equation, it is easy to arrive at the conclusion that no comparison can be made between the dehydrochlorination reaction under elevated temperature and the reaction caused by alkaline elimination. From the point of view of molecular collision dynamics, the reaction rate depends, among other parameters, on the size of the molecules, the collision energy (both values are included in a so-called collision cross-section) and the energy of chemical change. All these values are entirely different in both cases, especially because in alkaline elimination one reagent is a small molecule of KOH.

Additional data of interest on alkaline dehydrochlorination are found in the work by Shindo,[12] who monitored the unsaturation formation rate during reaction by UV spectroscopy. Figure 9.4 shows how the molecular weight of polymer determines the rate of double bond formation, depending on reaction time.

The elimination rate increases with increasing molecular weight, which differs substantially from the results obtained for thermal degradation of PVC. For the discussion of results, Shindo derived the following equation:[12]

$$\frac{[\eta]}{[\eta_0]} = \left[\frac{\langle R^2\rangle}{\langle R_0^2\rangle}\right]^{3/2}\left[1 - 0.584\sum_{1}^{\rho}\frac{n_{2i}}{D}\right]^{-1} \qquad [9.1]$$

in which:

$$\frac{\langle R^2\rangle}{\langle R_0^2\rangle} = \frac{\sigma'^2}{\sigma^2} - \frac{\sigma'^2}{\sigma^2}\left(\sum_{1}^{\rho} n_{2i}/D\right) + \frac{a^2 l - \cos\Theta\sum_{1}^{r} n_{2i}}{a^2 l + \cos\Theta\sigma^2 2D} \qquad [9.2]$$

where:

$<R^2>$	the mean-square end-to-end distance of the dehydrochlorinated chain,
$<R^2_0>$	the mean-square end-to-end distance of the initial chain,
σ	factor due to the hindrance of internal rotations (for PVC=1.83),
σ'	factor due to the hindrance of internal rotations in dehydrochlorinated chain,
n_{2i}	number of conjugated double bonds in sequence,
D	degree of polymerization,
a	length per conjugated double bond unit,
l	bond length,
Θ	supplement of the bond angles,
$[\eta]$	intrinsic viscosity of initial polymer,
$[\eta_0]$	intrinsic viscosity of dehydrochlorinated polymer.

Based on this relationship, the ratio $[\eta]/[\eta_0]$ has been calculated and compared with values of that ratio obtained from experiment with a good agreement. The following polyene length distribution and physical properties have been proposed for PVC extrudate as shown in Table 9.2.[30]

Table 9.2. Polyene length distribution in PVC extrudate. [Data from Ref. 30.]

n	λ_{max}, nm	ε_{max}, 1000/mol cm
4	312	73
5	329	121
6	345	138
7	371	174
8	395	204
9	421	233
10	445	261
11	467	292
12	485	320

The values of λ_{max} slightly vary in different papers.[16,19,30] Evidently, isolated double bonds and diene sequences cannot be seen from the spectra, and trienes can be detected only with difficulties.

Wiersen and Flodin[16] did not observe the crosslinking reaction in their experiment on alkaline elimination of HCl. The only reason for molecular weight change was chain scis-

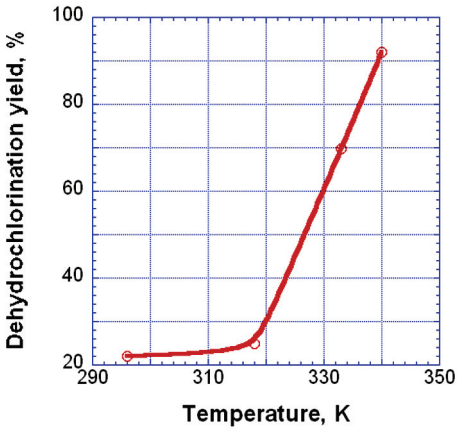

Figure 9.5. Dehydrochlorination yield by reaction with alkoxide (BuOK) vs. temperature. [Data from Hollaender, A.; Zimmermann, H.; Behnish, J., *Eur. Polym. J.*, **27**, 9, 959-963, 1991.]

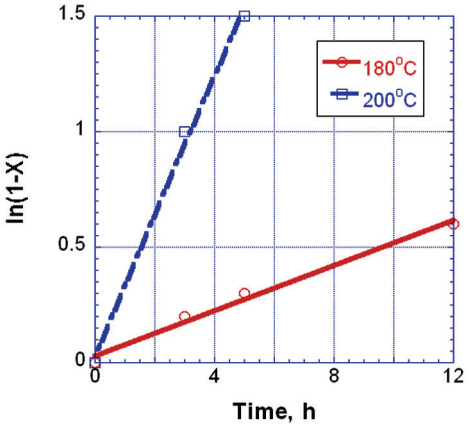

Figure 9.6. First order plot of dehydrochlorination for rigid PVC pellets in 3 M NaOH. [Data from Shin, S. M.; Yoshioka, T.; Okuwaki, A., *Polym. Deg. Stab.*, **61**, 2, 349-353, 1998.]

sion, the rate of which could be restricted to one or below per polymer chain with samples of low conversion. Ozonolysis was performed to determine the length of polyene sequences, followed by determination of molecular weight distribution. Comparing the molecular weight distribution of the initial polymer to the polymer being dehydrochlorinated and subjected to ozonolysis, Wiersen and Flodin[16] concluded that active centers in which the elimination reaction was initiated were randomly distributed. Hence, the reaction started at some weak points of the polymer chain and continued to produce longer sequences in the further course of the process. The places of initiation were distributed at an average distance of 150 carbon atoms for suspension polymer, and the product of the elimination reaction could be described by the general formula:

$$\sim\!\!\sim\{(CH_2CHCl)_{70}(CH{=}CH)_{1\text{-}14}\}_m\sim\!\!\sim$$

It was concluded that only a few sequences had more than 15 double bonds, but the data presented and the methods used cannot guarantee that such a conclusion is valid, as practically speaking, more than 11 bonds in conjugation cannot be detected on the UV/visible spectrum.

Figure 9.5 shows data for PVC reaction with alkoxide. After the temperature exceeds the melting point of the alkali metal (potassium: 336 K), a rapid increase in the reaction rate is observed and reaction yield begins to increase linearly. It only takes about 2 hours to complete dehydrochlorination at the highest temperature studied.[18]

Figure 9.6 shows that dehydrochlorination of rigid PVC pellets is a first order kinetical process which can be expressed by the following equation:[6]

$$-\ln(1 - X) = kt \qquad [9.3]$$

where:

X	dehydrochlorination degree,
k	rate constant,

t reaction time.

The mechanism of the elimination reaction is still unresolved. Wiersen and Flodin[16] concluded that dehydrohalogenation of alkyl halides occurs according to the E_N2 mechanism. It is believed that at the beginning of the dehydrochlorination, chlorallyl structures are formed in the PVC backbone by the statistical random attack of the base.[18] Because of the lower stability of a chlorallyl structure compared with a random vinyl chloride unit, further elimination of hydrogen chloride occurs, most likely by zipping reaction.[18] Therefore, even at an early stage of dehydrochlorination, long sequences of conjugated double bonds are formed. There is evidence for an E_N1 mechanism of HCl elimination from chlorallyl structures as the main reaction for growth of polyene sequence.[18]

Diels-Alder inter- and intramolecular cyclization is one of the side reactions which lowers polyene conjugation.[4]

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10

Analytical Methods

This chapter includes methods used in testing PVC and its compounded formulations with and without stabilizers. The most popular methods used in PVC thermal degradation and stabilization studies are discussed to show:

- suitable use of analytical technique,
- applications and expected results,
- limitations and errors.

10.1 HEAT STABILITY TEST

10.1.1 SAMPLE PREPARATION

Sample selection consists of two important factors:

1. The method of polymer synthesis.
2. The method of specimen preparation.

Studies conducted in the area of polymer degradation and stabilization are designed mainly to facilitate practice; therefore, the industrial product of vinyl chloride polymerization (specifically used in practical formulation) offers the best choice. At the same time, all industrial polymers contain polymerization additives, and they are mixtures of a broad spectrum of molecular weights, which raises concern that they may interfere in studies being conducted. We therefore have a choice of three other methods:

- polymer purification,
- polymer fractionation,
- polymerization under laboratory conditions.

Polymer purification is done either by the Soxlet extraction with methanol and hot water washing or by tetrahydrofuran dissolution and methanol precipitation and washing. The first method seems to affect the initial properties of polymer less, since only limited extraction of low molecular fractions of polymer was reported, while the second method leaves behind trace quantities of solvent (THF), which may participate in further photooxidation and thermooxidation processes as previously discussed. In addition, dissolution of polymer changes its original morphology and structure of polymer particles. Polymer fractionation has a similar impact on results since fractions are usually obtained by gradual precipitation of polymer from its solution by periodic dosing of non-solvent. As a result of this process, one can obtain samples of a narrow range of molecular weight distribution.

Laboratory synthesis may lead to various effects, depending on the kind of studies being conducted. One should realize that such synthesis leads to polymer that is not directly comparable with industrial products, and hence the conclusions can be atypical.

The great majority of polymer samples are industrial products not subjected to any treatment before they are formed into the intended specimen shape or formulation. Only in special cases was the polymer specimen obtained by laboratory synthesis. This includes studies on tacticity effect and studies of labile structures wherein a larger variety of tacticity or labile structures are needed than that offered in the existing industrial products. Purified samples of polymer were used occasionally in studies on thermodegradation kinetics, stabilization and photolysis. The above discussion shows that the authors confined themselves to a more practical approach. Selection of a specific polymer grade is related to the expected supply in a global economy.

Considering the method of specimen formation, we have a wider variety of techniques:

- film cast from solution,[1-4]
- polymer solution,[5,6]
- powdered polymer,[7]
- blend of polymer with other ingredients,[8]
- extruded specimen,[9-11]
- plastisol spreading and thermal curing,[12]
- compression molded sheet,[7,9,13]
- calendered sheet,[14]
- twin-roll milling,[7,13,15]
- cutting from manufactured product,[16-18]
- plastograph mixing,[19]
- IR die pellets.[20]

The form of the specimen depends in the first place on the analytical method used in the course of studies. This is why a large number of specimens used in the studies were obtained in the form of solution or the film cast from solution, usually from tetrahydrofuran. If the method used in investigation demanded a sample of high transparency, which cannot otherwise be achieved without advanced changes that are caused by thermal degradation, the solution casting was selected. At the same time, every investigator using samples treated with solvent was probably aware that the traces of solvent left in the specimen affect the course of the photooxidation reaction; therefore, in these studies the type of analytical method played a predominant role. The use of solution, polymer cast from solution, or polymer precipitated from solution is the most risky method of sample preparation, and therefore, it should be used only when other methods fail to provide required sample specification. In such cases, there are several solvents in common use, including: tetrahydrofuran, dichloroethane, 1,2,4-trichlorobenzene, dimethylformamide, cyclohexanone, hexamethylphosphotriamide, and pyridine. From the point of view of its effect on initial polymer properties, cyclohexanone should be the first choice; unfortunately, it has too high a boiling temperature and viscosity, which rule out its common use. Tetrahydrofuran is the most commonly used solvent, even though it is the most inadequate due to its tendency to oxidation and peroxides and carbonyls formation.[4] The most important factors to consider are related to the solvent purification,[21] but at the same time one should bear in

mind that further use of a specimen in the presence of oxygen has a detrimental effect on its condition.

The original powder form of PVC is the most appropriate for further studies, but in the thermal degradation test, the size of the grains plays an essential role. In consequence, the sample should be repeatedly selected for a narrow range of grain size or sieved prior to its use. In some studies, samples were prepared using an IR die for pressing pellets.[20] Here the thermal effect is minimal; therefore, the sample could be regarded as similar in properties to the original form. The disadvantage of this method is that the sample is fragile and lacks transparency. Another moderately heat-treated sample could be formed from plastisol at temperatures much below the gelation point (about 373K), but this technique is limited only to the studies, which call for formulation with plasticizers.[12]

Film calendering, injection molding, extrusion, and compression molding are also frequently applied. It is understood from the principles of these methods that thermal changes have been introduced into the material in its initial form. In order to achieve repeatable results, a strict regime of processing is applied in which temperature is controlled, as is shear rate, which indirectly is also related to the level of heat treatment the sample obtains. Although these methods are the most process-oriented, they may introduce quite advanced changes since it is not exceptional for the sample to be processed for 10 min at 453K. In addition, before any of these methods is applied, the material components must be homogenized which is done in most cases by roll milling (usually at 433-443K for 5-8 min).[7,13,15]

A group of techniques are applied when polymer is studied in the presence of additives, as for example, in the stabilization research. In this case, good dispersion of additives is very important. Usually the additive has a different bulk density than polymer; so mixing in a mortar alone may prove inadequate. Blending the mixture in high speed mixers[9] with temperature increase (up to 393K) gives good results in the distribution of additive, but some thermally induced changes may occur which affect further results. The most even coating of polymer can be achieved by dissolving the additive in solvent that does not interact with polymer. But such an approach should not include the polymer solubility alone. In one study, the stabilizer was dissolved in ketone, which is known to be able to interact with polymer, and such a practice is too risky because it may change grain morphology.

Some studies use final products without having any knowledge of previous processing because either different commercial products are compared or the possibility of recycling is investigated.

From the above discussion, one can easily come to the conclusion that sample preparation alone can be at least as important for the results obtained as the measuring technique itself. Therefore, the method of sample preparation should not only be cautiously selected but the results scrutinized, investigating the possible effect of the method on studies being conducted. It should be also underlined that experimental papers should include full information about sample preparation (which frequently is missing, but it is very helpful for enabling a reader to understand the results).

10.1.2 KINETIC STUDIES OF DEHYDROCHLORINATION

Measurements of PVC thermal degradation are the most important for the evaluation of polymer thermostability. A variety of methods are known, but only a few papers give details of equipment construction, so practically every laboratory has been using its own model, especially since until quite recently there was no commercial equipment for this study. The measurement of PVC thermal degradation is very simple in principle but it is complicated by numerous parameters.

The simplest methods, designed some years ago, such as determination of initial period by Congo red paper and solution[22,23] or by $AgNO_3$ solution,[23] are not frequently used. The oven test of sample color change under heat treatment only has industrial application.[24,25] The same is true of the method for measuring the electrical conductivity of a sample.[26-28] Pressure measurement of gaseous products emitted by the sample is not used because of the interference of HCl's catalytic effect.[29,30]

There is continuous interest in thermogravimetric analysis, TGA, and differential thermogravimetry, DTGA, although they should be only used for samples free of volatile substances, e.g., plasticizers.[50-51] The equipment is readily available, automatic, and precise, but results are frequently confusing because of the interference of volatile components other than HCl such as moisture, solvents, and additives.

The original method of HCl monitoring was used in Australia,[56] where the IR spectrophotometer was applied to detect HCl evolvement at 2963 cm^{-1}. In another development, Guyot and Bert[48] applied differential conductometry.

The most commonly used methods are those in which a sample is subjected to isothermal heating, and the evolved hydrogen chloride is monitored after absorption in distilled water. HCl determination is done by one of these methods:

- potentiometric titration,[31,32]
- argentopotentiometric titration,[33-36]
- pehametric,[37-41]
- conductometric measurement.[25,31,42-49]

The last method, conductometric measurement, is by far the most popular.

The detection limits for potentiometric and argentopotentiometric titration is 10^{-2}% of total HCl in the sample. In the case of thermogravimetric measurement, the same value equals 1.2×10^{-1}% for a 5 mg sample. For the pH-metric method, the suggested detection limit of 10^{-4}% seems to be overestimated.[38] In the case of the conductometric method, Abbas[49] claimed to obtain a detection limit of 10^{-4}%. If we use a conductivity meter that can measure 0.01 S for a sample of 0.1 g, we can detect 3.3×10^{-3}% HCl, which is equivalent to 9.3×10^{16} HCl molecules evolved, meaning that roughly every tenth chain of average molecular weight of 8×10^4 had split off one molecule of HCl before we were able to detect it.

The sample and the equipment construction are very important for precision of studies. It is thus essential to discuss them in full available detail.

The amount of sample taken for measurement is quite important. By increasing the sample amount by the order of ten, one may increase sensitivity by the same value, but at the same time, thermal balance, i.e., isothermal conditions, will take longer to attain. Even

more important is the sample thickness. Polymer, under the conditions of measurement, is of high and increasing viscosity, and HCl escapement becomes more difficult if viscosity is high. Unless taken by a carrier gas into the measurement cell, HCl stays in or around the sample, which causes uncontrolled conditions of degradation with variable extent of catalytic influence of hydrogen chloride on the degradation rate.

The other essential factor concerns the material from which the reaction vessel is made. Contact between the sample and the reaction vessel's surface may produce an additional unexpected effect, i.e., concerted elimination or the process of initiation and termination of HCl split off, which is catalyzed by reactor walls. This might cause experimental error, because in most cases the experimental vessels are composed of Pyrex glass, which may contribute to the wall-catalyzed effect. Pyrex glass reactors might be prepared for degradation studies of halides by formation of carbonaceous coatings. For degradation at temperatures below 583K, PTFE-coated reactors provide the most inert surface.[57] One should remember that polytetrafluoroethylene has a very low thermal conductivity coefficient, therefore the thickness layer should be minimal. Polytetrafluoroethylene is also useful in maintaining a clean surface before a new sample is introduced.

The dimensions of the degradation vessel are also important. The size of the reaction vessel does not practically affect the character of carrier gas flow, since the value of Reynolds's number is very low ($\sim 1 \times 10^{-3}$); therefore, carrier gas has laminar flow. Under such conditions of flow, the heat exchange rates are very poor. The volume of the reaction vessel is important because, together with carrier gas flow rate, it determines the rate at which the atmosphere surrounding the sample is exchanged, which is important for diminishing the catalytic effect of HCl mentioned above. It is suggested that the carrier gas replacement frequency should be in the range of 5-20 total reaction vessel volume exchanges of carrier gas per minute. One should keep this value as high as possible, not only to diminish the catalytic effect, but also to achieve better mixing of gas inside the reactor and faster transportation of HCl to the conductivity cell, thus providing for its faster detection.

Isothermic conditions under which the sample is degraded are probably the most difficult to achieve, and they contribute to most data errors. Vymazal[58] has described a method of calculation of the correction factor for non-isothermal conditions. He has also given the values that characterize the rate of temperature increase in the sample, as shown in Table 10.1.

Table 10.1. Sample temperature increase during degradation measurement of 0.2 g of PVC powder. Carrier gas flow rate: 330 cm^3/min. [Data from Ref. 58.]

t, min	T, K	t, min	T, K
0	293.0	7	451.5
1	373.0	8	452.4
2	405.0	9	452.6
3	428.0	10	453.0
4	443.6	12	453.1
5	448.0	14	453.0
6	450.4		

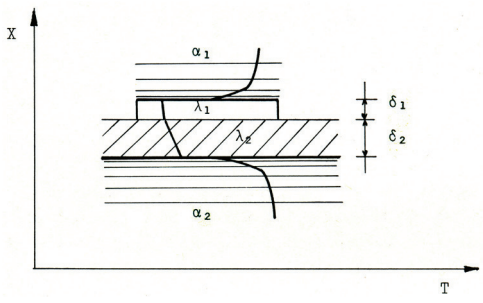

Fig.10.1. Sample heating diagram.

Assuming that a tolerance of 1K have to be achieved, we may see from the data that isothermal conditions are attained after 8 mins, which means that, depending on PVC type for degradation measured at 453K, from 4 x 10^{-3} to 2.6 x 10^{-2}% of the sample would have already been degraded. In other words, from 2.2 x 10^{17} to 1.3 x 10^{18} HCl molecules were produced, which means that every statistical chain had already formed one double bond. Wang[41] claims that the tolerance of 1K is reached in 4.5 mins after inserting the sample, while Abbas[49] claims that 2 mins are needed to approach a temperature of 463K by 1K difference. Based on these data, it seems important to discuss the problem of isothermal conditions in detail. The conditions of sample heating once the sample has been placed in the reaction vessel can be illustrated by Figure 10.1.

The sample is heated from the top by gas, and the process of heat exchange is limited by values of convection heat transfer coefficient, α_1, and by the conductivity of the sample, λ_1. From the bottom, the sample is usually heated by hot oil, and the process is controlled by convection heat transfer coefficient, α_2, and conductivities of the glass wall and the sample, λ_2 and λ_1, respectively.

In order to obtain near isothermal conditions of sample degradation, we must try to achieve the highest values for α_1, α_2, λ_1, and λ_2, δ_1 and δ_2 should be as small as possible. T_1 (temperature of gas) and T_2 (temperature of heating oil) should be almost equal. We are limited in selection of the values of λ_1 and λ_2 as PVC conductivity depends on the sample and cannot be improved. Only λ_2, the conductivity of vessel material, can be improved by material selection. A change in α_1 can only be effected by a very drastic change in the carrier gas flow rate, which requires very efficient heating to maintain gas temperature. Also, δ_1 cannot be fully controlled (only initial thickness can be selected by the experimenter), because under measuring conditions the sample becomes a plastic material and its thickness changes, depending largely on its viscoelasticity and the surface tension of PVC melt. What we can do is to limit the α_2, δ_2, and $(T_1 - T_2)$ difference. The overall heat transfer coefficient is given by the function below:

$$\alpha = f(w, d, L, \eta, c, \lambda) \qquad [10.1]$$

where:

w	rate of flow of fluid,
d, L	linear dimensions of the reaction vessel,
η	fluid viscosity,
c	specific heat of fluid,
λ	conductivity of fluid.

Therefore, we should increase w and λ, and decrease c and η.

Unfortunately, the practical values of w in an oil bath cannot be increased drastically enough to achieve the change of flow character, i.e., from a laminar to a turbulent one. One should, therefore, try to experiment with the oil used in the oil bath in order to opti-

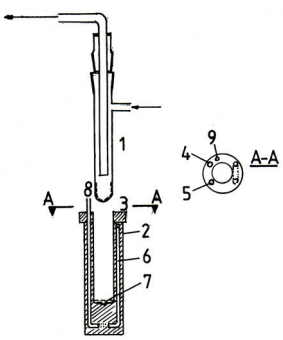

Figure 10.2. The construction of the degradation vessel. 1 – glass degradation vessel, 2 – brass block, 3 – PTFE insulating ring, 4 – carrier gas inlet, 5 – carrier gas outlet, 6 – gas heating channel, 7 – silicon oil, 8 – PTFE coating, 9 – thermocouple. [Wypych G., Drawing of the original equipment built in 1978].[59-61]

mize the values of λ, c, and η. Another possibility was used in this author's laboratory.[59] As convection in comparison to conduction is a rather slow process of heating, one may foresee that if the bottom of the sample is to be heated through conduction, the results should be much better. Figure 10.2 shows the details of design of such equipment. The element shown in Figure 10.2 is part of the measuring set shown in Figure 10.3. The glass reaction vessel has a diameter smaller by 0.2 mm than the internal diameter of the brass heating block; therefore, the glass vessel and brass block are in almost direct contact.

To improve the conditions of heat exchange still further, a small amount of silicon oil is placed inside the brass block to seal both surfaces. A very thin oil layer transfers the heat primarily by conduction because the "wall layer" is diminished.

In order to complete our discussion of the problems connected with measuring the thermal degradation process of the PVC sample, we should mention briefly some other obvious but important points:

- The distilled water used in conductivity measurements should be of the highest possible quality.
- The residual conductivity of water after saturation with inert gas should be constant before measurement starts and at least less than 0.5 μS.
- Thermostating of water and the use of automatic thermal compensation is important in obtaining reliable data.
- A standard curve of at least 30 points of different HCl dilutions with statistical approximation should be carefully prepared.
- Sample loading time should be diminished.
- One should not allow a higher error than 0.02% in sample weighing.

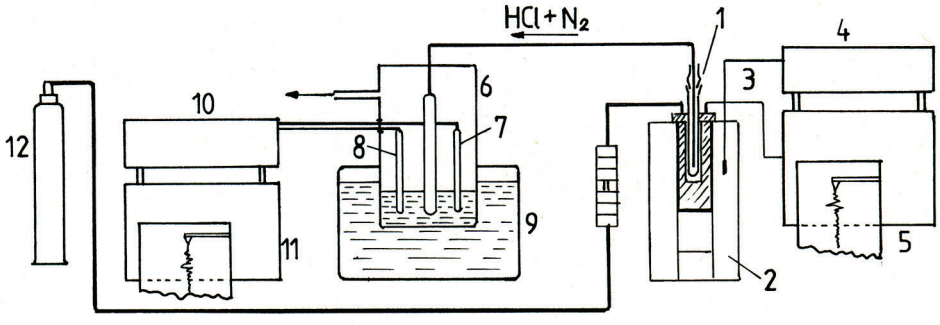

Figure 10.3. PVC degradation measuring apparatus. 1 – degradation vessel, 2 – furnace, 3 – thermocouples, 4 – temperature regulator, 5 – temperature recorder, 6 – conductivity vessel, 7 – conductivity probe, 8 – temperature sensor, 9 – thermostat, 10 – conductivity meter, 11 – conductivity recorder, 12 – carrier gas cylinder, 13 – rotameter. [Wypych G., Drawing of the original equipment built in 1978].[59-61]

- All glassware and tubing should be made out of inert material and cleaned and dried after each measurement.
- Carrier gas should be transferred through the system by overpressure rather than by using vacuum pumps, because in the latter case, during the time of sample loading, water is being saturated by carbon dioxide, which influences conductivity measurement.

Metrohm has introduced automatic equipment Metrohm 763 PVC Thermomat which includes in the design the above observations. The equipment is PC controlled and permits PVC testing in accordance with the standardized methods.[24,37] Two heating blocks contain 8 samples, which can be tested at two different temperatures with management of each sample by computer according to the selected conditions. Analysis capacity can be increased to 32 samples and up to eight different temperatures by connecting up to four PVC thermomats to a PC. Samples are tested in disposable reaction vessels. The availability of commercial instrument should contribute to improvement in data quality and uniformity.

10.1.3 DEHYDROCHLORINATION RATE AND OPTICAL CHANGES

PVC thermal degradation studies are the most frequently conducted based on the measurements of evolved HCl and sample color change. The amount of HCl evolved during thermal degradation is the most frequently used method in both industry and research laboratories, yet it does not measure the most essential factors for the preservation of the properties of polymer – mechanical strength and color. The situation is further complicated by the fact that there is no direct correlation between the amount of evolved HCl and the color stability of the sample.

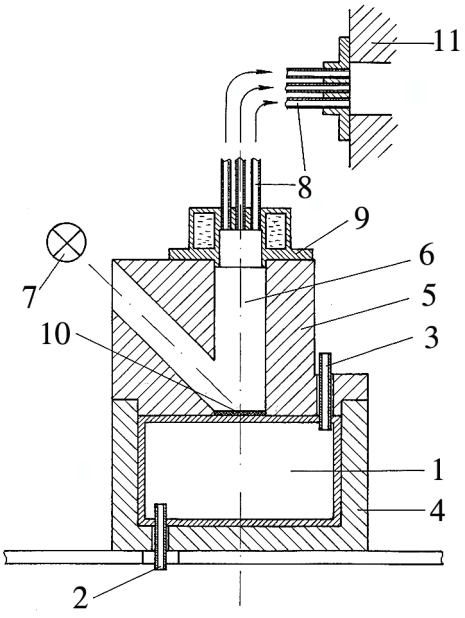

Figure 10.4. Color stability and dehydrochlorination oil-heated device. [Adapted from Wypych, G.; Kozlakowski, K.; Krzeszewski, L.; Roszkowski, W., **UK Patent Application, GB 2 174 800 A**. Color stability measuring device. Date of filling May 7, 1985.]

In studies on PVC thermal stabilization, color retention is regarded as the most important factor used to control the suitability of stabilizer formulation. In order to understand the mechanism of action of stabilizers, it is necessary to know results from both tests (see more on this subject in the next chapter). It is even more essential to have this information from measurements done simultaneously for the same sample. Figure 10.4 shows schematic diagram of a device capable of measuring color change and dehydrochlorination simultaneously for the sample. Equipment given in Figures 10.4 and 10.5 was used for studies of per-

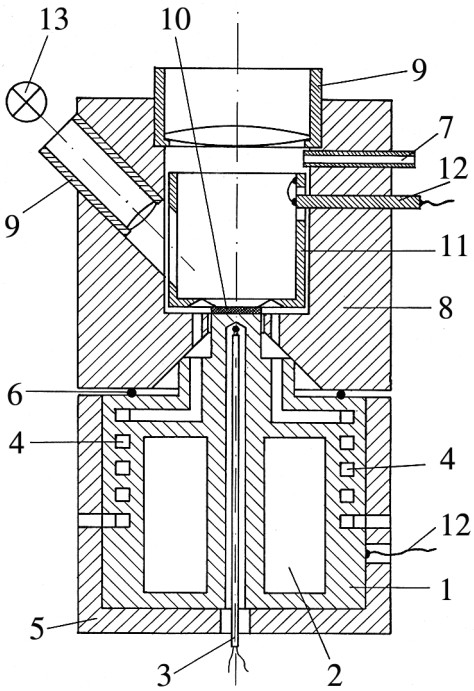

Figure 10.5. Color stability and dehydrochlorination electric element-heated device. [Adapted from Wypych, G.; Kozlakowski, K.; Krzeszewski, L.; Roszkowski, W., **UK Patent Application, GB 2 174 800 A**. Color stability measuring device. Date of filling May 7, 1985.]

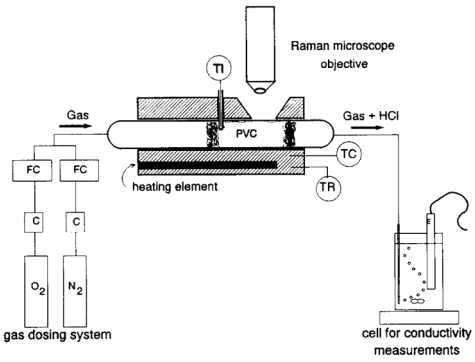

Figure 10.6. Raman/dehydrochlorination apparatus. [Adapted, by permission, from Hillemans, J. P. H. M.; Colemonts, C. M. C. J.; Meier, R. J.; Kip, B. J., *Polym. Deg. Stab.*, **42**, 3, 323-33, 1993.]

formance of almost 150 thermal stabilizers reported elsewhere.[60]

Equipment in Figure 10.4 comprised of a heating chamber (1), equipped with an oil inlet (2) and outlet (3), bottom insulating cover (4), an upper insulating cover (5) containing light pathway (6), a halogen lamp (7) with a current stabilizing circuit up to 0.01 V (in order to obtain stable beam intensity), and a set of light pipes (8) mounted in a water-cooled mounting (9) in order to protect them. Light from the halogen lamp, dispersed on the sample (10) was normally conveyed to an AA spectrophotometer (11), and measured at 500 nm, converted to reflectance, and continuously recorded, resulting in a graph of reflectance versus time.

The measuring device shown in Figure 10.5 is comprised of a metal block (1) with a heating element (2), a thermocouple (3) which measures and regulates temperature, a carrier gas heating channel (4), lower insulating case (5), gas-tight gasket (6) in order to maintain the atmosphere of gas (air, N_2, etc.) and to allow for HCl measurement, carrier gas sample outlet (7), upper insulating case (8) containing the light pathway and part of the optical system (9). Light signal from the lamp (13) dispersed on the sample (10) is conveyed through an optical system to a monochromator and converted to an electrical signal by the detector. The color of the sample is expressed in CIE-tristimulus values. The evolved HCl is measured by the conductivity of water, through which outlet gas is percolated. Electric conductivity of the sample (10) is measured continuously between the upper sensor ring (11) and a metal block (1). The electric signal is taken from electrodes

(12). The upper part of metal block, made out of brass, is gold-plated like the upper cylinder (11) in order to protect it against the corrosive action of HCl. [62]

Hillemanns *et al*.[63] developed equipment to follow the formation of polyenes *in situ* by Raman spectroscopy with simultaneous measurement of the HCl evolution by a conductometric method (see Figure 10.6). PVC powder was placed in a quartz reactor tube (diameter of 10 mm) with a thermocouple placed halfway along. The reactor was enclosed in a thermostated copper block.[63] An identical setup was used with a UV/vis reflectance spectrophotometer.[63]

10.1.4 DEGRADATION IN SOLUTION

Some research groups use PVC solutions and expose them in ultraviolet reactor manufactured by Southern New England Company.[64-8] The types of reactor used include Rayonet RS (not manufactured any longer) RPR 100, RMR-200, and RMR-600. The reactors can be equipped with different radiation sources (simulating different regions of sun radiation), temperature is not controlled. Samples are placed in a quartz tube enclosed for the time of irradiation.

10.2 THERMOGRAVIMETRIC ANALYSIS

10.2.1 DIFFERENTIAL SCANNING CALORIMETRY, DSC

DSC is a general purpose analytical method in polymer studies but frequently and successfully used in PVC degradation related studies of the following topics:

- degree of gelation and fusion,[69-71]
- melting point of stearates and consequently effect on their properties,[72]
- melting point determination of stabilizers,[73]
- effect of plasticizer addition and loss on glass transition temperature,[74-75]
- stabilizer distribution in polymer blend,[76]
- decomposition and concentration of azodicarbonamide and performance of kickers,[77,78]
- decomposition of epoxidized soybean oil,[79]
- crystallinity of PVC,[80,81]
- glass transition temperature of PVC,[82,83]
- gauging the mechanically induced stress in PVC when oriented below glass transition temperature,[84]
- *cis/trans* isomerization,[85]
- activation energy of thermooxidative degradation,[86]
- oxidative induction time.[87]

10.2.2 MASS LOSS

Mass loss by TGA is one of the most popular methods of study of PVC thermal degradation in spite of the fact that it has many drawbacks and produces results which are difficult to interpret.

Typical parameters of TG analyzer are as follows:

temperature range	from -120 to 1500°C
temperature reproducibility	+/- 0.1%

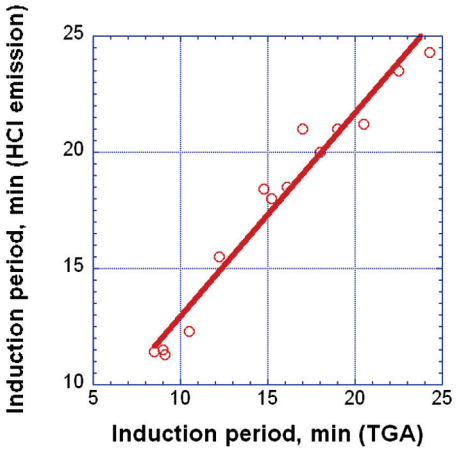

Figure 10.7. Induction period of PVC degradation determined by TGA and HCl emission. [Data from Benavides, R.; Edge, M.; Allen, N. S., *Polym. Deg. Stab.*, **49**, 1, 205-11, 1995.]

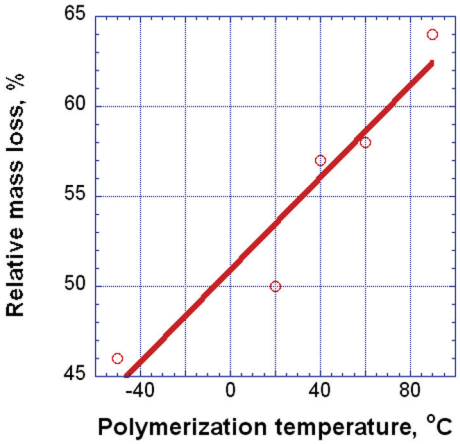

Figure 10.8. Relative mass loss in the first stage of PVC degradation in Hi-Res TGA vs. polymerization temperature of the polymer tested. [Data from Gonzalez, N.; Mugica, A; Fernandez-Berridi, M. J., *Polym. Deg. Stab.*, **91**, 4, 629-633, 2006.

programmable scanning rates	from 0.01 to 300°C/min
balance capacity	3 g
measurement range	+/-200 mg
resolution	0.03 µg
detection	1 µg

The above characteristics show that instrument performance is excellent, including high repeatability and low error, in addition to the simplicity of operation and a low time-consuming sample change. The instrument can be run under air or any inert gas. Also, it can be interfaced with mass spectrometer, gas chromatograph, or IR spectrophotometer. This contributes to a magnitude of options.

There also are some important disadvantages the method suffers from. The method measures weight loss under some selected heating conditions. If PVC alone is being heated, the initial weight loss is caused by HCl emission but it is also known that many volatile organic substances are formed at different stages of degradation and their emission overlaps with emission of HCl which makes results difficult to interpret.

Heating rate can be selected by the operator but the heating rate influences the dehydrochlorination rate.[88] This complicates the use of results because results from different studies, using different settings, cannot be directly compared.

Benavides *et al*.[89] compared the initial period of different samples (different stabilizers, their concentrations, and temperatures) measured by TGA and HCl evolution (Figure 10.7). In the majority of cases, the induction period determined by TGA is 3-4 min shorter than the induction period determined by HCl evolution. It is suggested[89] that the shorter induction period determined by TGA is caused by the prolonged presence of HCl (and thus more extensive catalysis) because of less efficient removal of HCl in thermogravimetric equipment.

In the use of Hi-Res TGA for PVC degradation, four different stages of weight loss were singled out.[90] The first stage is believed to be related to the presence of labile groups. Figure 10.8 shows the relationship between polymerization temperature and relative mass loss in the first step.[90] TGA test results correctly predict the influence of polymerization temperature on the degradation rate, which shows that interesting data can be obtained by this method if PVC is studied alone (without additives).

In systems containing plasticizers, extensive loss of plasticizer begins to occur at 210-220ºC, which is above typical test temperatures of PVC degradation.[91] But it was determined that at 180ºC, 1% of DOP has been already lost, which is a very high number compared with potential loss of HCl.[92] This shows that formulations with plasticizers require a very large correction (if this correction is ever possible). It was found[93] that plasticizer evaporation makes a surface porous, which affects the dehydrochlorination rate, especially in the presence of oxygen.

TGA study of plasticized PVC was too complicated to interpret therefore spectroscopic PVC degradation kinetics was measured by monitoring absorbance of polyene sequences formed.[94] Unlike TGA results, spectroscopic studies were not affected by plasticizer loss.[94] TG/FTIR analysis of co-pyrolysis behavior of PE, PVC and PS was conducted.[95] The volatile products were analyzed to investigate the interaction of the plastic blends during the thermal decomposition process.[95] TG–MS analysis of nitrile butadiene rubber blends with PVC was studied.[96] The most remarkable change was the absence of HCl from decomposition products in the presence of the $Mg(OH)_2$.[96]

In summary, TGA is simple to use but it should be better avoided in PVC thermal degradation studies because many confusing findings are possible with this method.

10.3 COMBUSTION

Four methods are used in the evaluation of burning behavior of PVC, including:

- char formation,
- limiting oxygen index, LOI,
- smoke density rating, SDR,
- cone calorimetry.

The last three methods are standardized and references to standards are included in the last section of this chapter. Char formation can be determined by TGA experiments but the sample is very small, which affects accuracy and mechanisms of degradation. A method was developed[97] in which a sample (usually about 0.5 g) of the polymer formulation is placed in a platinum crucible which has a tight-fitting lid with a small circular hole (1 mm in diameter) in the centre that allows volatiles to escape during heating. The crucible is supported in a stainless steel frame which locates the sample exactly in the centre of the temperature controlled zone of a vertical tube furnace.[97] Suggested temperature is 650°C (a temperature typically occurring during the “flashover” conditions in a real fire).[97] The technique has been found to give extremely accurate and reproducible data.[97]

Char yield values can be calculated from the following equation:[98]

$$\text{Char yield} = w_2/w_1 \times 100\% \qquad [10.2]$$

where:

w_1 weight before combustion,
w_2 weight after combustion.

TGA-MS studies were also conducted on flue gases from combustion to determine their composition.[99] HCl and benzene were found to be main products of combustion but about ten other products were determined.[99]

Toxic effluents (polychlorinated dibenzo-p-dioxins, polychlorinated dibenzofurans, and polycyclic aromatic hydrocarbons), such as released from PVC carpet burning, were analyzed using filter/absorbent methods, toluene extraction and subsequent analysis by GC-MS.[100]

10.4 OPTICAL PROPERTIES

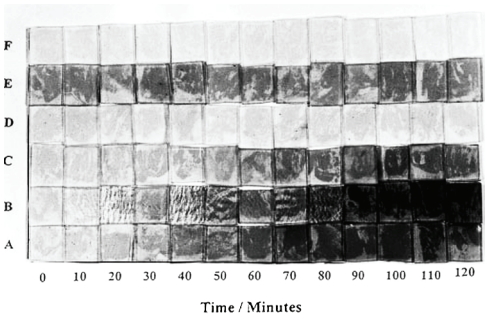

Figure 10.9. Oven aging results. [Adapted, by permission, from Fiaz, M.; Gilbert, M., *Adv. Polym. Technol.,* **17**, 1, 37-51, 1998.]

Color change, gloss, and haze are the optical properties which are frequently investigated in the relationship to PVC stability during exposure to heat and various forms of radiation, including outdoor exposures. These studies frequently do not results in understanding of mechanisms which cause the changes but demonstrate that something must be changed in the formulation to improve optical qualities, which are obvious signs for customers that the product is not performing well.

Two methods of color change monitoring are in common use; both involve the heating of test samples at a selected temperature for varying times. Samples might be exposed either to heat or radiation. In the case of thermal degradation, samples are most frequently exposed in an oven but dynamic tests also are common, such as twin-rolling at degradation temperature. In one method, samples are visually inspected and compared with results for other formulations. Figure 10.9 shows the typical method of reporting such data.

In a modernized technique, the color of samples is measured by adaptation of the CIE tristimulus values method and given in a numerical form, allowing for comparison. The latter method, although the best technique now available, has a few serious deficiencies. It does not allow for kinetic measurements, since samples must be prepared by periodic heating and measured externally. Periodic heating disturbs isothermal conditions; therefore, the method cannot be used for studying changes of "early color".

Sample color change is frequently expressed by a yellowness index, YI, given by the equation:

$$YI = 100\frac{1.28X - 1.06Z}{Y} \qquad [10.3]$$

where:

X,Y,Z CIE tristimulus values.

Samples with YI = 0 did not change color, those having YI > 0 are discolored towards yellow, and those having YI < 0 are discolored towards blue.

The best application of this method is in measuring initial color change, since the higher degradation stages may not be recorded with initial sensitivity. Using this method, one should always have a standard sample thickness and a standard background on which the sample is placed for measurement, bearing in mind that practically every sample is transparent; therefore, both parameters affect the measured value. This method has one serious shortcoming, since it can be operated only on a periodic basis. The results would be more useful if they were comparable with results of other measurements, e.g., HCl emission rate (see Section 10.1.3). On the other hand, it is already a step in the right direction, since we are able to observe changes by more objective instruments than the human eye.

One of the most widely used methods of color measurements is the CIELAB system (L*, a* and b* system).[102]

Still another technology was employed for measurement of color changes. Sample strips were thermally degraded in a Mathis oven at 177, 190 or 204°C and Red, Green and Blue (RGB) values were measured with a scanner using the FloScan program (Dr. Stapfer GmbH, Germany). The accuracy of the measured Red, Green and Blue (additive colors, RGB) as well as Cyan, Magenta, Yellow (subtractive colors CMY) values was tested using 20 color standards from ColorChecker (Gretag-Macbeth Co.) with a good correlation obtained.[103] This method continues to have the same drawbacks as previously described but is an improvement over yellowness index because it can better express red, green, and dark colors.[103]

Gloss and haze are very popular indicators in paint testing, less so in PVC but in some studies of commercial products these two methods are being utilized. The last section of this chapter gives references to standardized methods of their measurement.

10.5 SPECTROSCOPIC METHODS

10.5.1 ATOMIC ABSORPTION, AAS

Atomic absorption is used to determine metals in PVC containing stabilizers[8,104-109,117] (and some other metal containing additives, such as fillers and flame retardants)[110-112] and leaching these additives to water and edible oil.[113-116]

The usual problem with stabilizer detection or determination begins with their extraction from the polymer compound and/or their solubility in a solvent used for analytical purposes. Phosphites or epoxidized compounds are easily soluble in most organic solvents. The same is true for liquid organotins which are also miscible with typical solvents. Once a liquid sample is obtained (e.g., by one of the methods given below), electrothermal

atomization is used.[104] Solid samples are pyrolyzed in a graphite furnace introduced in a pyrolytic graphite tube.[112]

Sample preparation for the determination of cadmium and lead requires 0.05 g of the PVC sample to be treated with 5 ml of DMF, heating gently (60-70°C) for 15 min.[104] Then 1 or 2 drops of acetic acid are added; after a few seconds the solution is completely clear. Once cool, the sample is diluted with acetone in a 20-ml calibrated flask.[104] This extraction method gave a relative standard deviation of determination usually well below 10%.

The following method was used to obtain a solution of aluminum and lead from a formulation containing large amounts of silicates.[105] The amount of 0.06 to 0.08 g of the PVC sample was weighted, placed in a 100-ml Kjeldahl flask.[105] 2 ml of concentrated H_2SO_4 were added and the contents heated for 15 min, first gently and then strongly.[105] Then, 5 ml of 30% H_2O_2 were added dropwise while continuing to heat.[105] The solution immediately becomes clear and a white precipitate appears.[105] The contents are boiled vigorously to eliminate the excess of H_2O_2 and left to cool and then diluted with about 25 ml of water.[105] *Aqua regia* was used to digest char samples left after PVC degradation to determine iron by AAS.[110]

The determination procedure using AAS, is straight forward and needs no special technique other than that used for general purposes.

Wavelength, nm[104,106]

aluminum	206.8-217.6
calcium	422.7
cadmium	228.8
lead	283.3
tin	286.3
zinc	213.9

Atomization temperatures, °C:[104,112]

drying step	70-120
charring step	400-450
pyrolysis (solid samples)	800
atomization step (solutions)	800-2000
cleaning step	2700

Interfering metals (permitted concentrations in $\mu g\ l^{-1}$):[104]

aluminum: tin, zinc (60); barium, cadmium, calcium, lead, magnesium (600)
cadmium: aluminum (0.01), lead, zinc (100)
lead: cadmium, magnesium, zinc (40); antimony, barium, calcium (400)

Maximum permissible concentration of PVC resin in sample: 20-70 $\mu g\ ml^{-1}$.[104]

Tin leaching studies from a water pipe indicated that extractable tin in PVC pipe is located at the surface of the pipe and the rate of diffusion of tin in the pipe to the pipe surface is negligible compared to the extraction rate of surface tin.[114] The amount of tin in water depends on conditions of water flow (turbulent flow extracts more tin) and pipe characteristics (new pipe vs. old pipe).[114]

10.5.2 AUGER

Auger electron spectroscopy could be useful in studies of PVC surface and in the depth analysis but an electron beam causes extensive degradation of PVC.[118-121] Dissociation of chlorine atoms occurs so rapidly that chlorine cannot be monitored.[119] HCl, CO, and CO_2 were found as volatile products of exposure to an electron beam.[120] Auger electron spectroscopy is more damaging than XPS and that is why XPS is used rather than Auger electron spectroscopy.[118]

10.5.3 ELECTRON SPIN RESONANCE, ESR

ESR is one of the most important methods in studies of mechanisms of degradation. Full account of its capabilities and achievements in UV degradation studies can be found elsewhere.[122] In PVC studies, ESR has been instrumental in many important findings, including:

- several mechanisms of degradation were developed with support of ESR data:
  - polaron mechanism of thermal degradation,[123]
  - mechanism of PVC stabilization by tin stabilizers,[124]
  - mechanism of chain branching explaining role of HCl,[125]
  - unimolecular mechanism of HCl splitting of,[126]
  - post-irradiation aging,[127]
  - peroxy-radical formation during thermal degradation,[128]
- identification of polyenyl radicals,[129]
- understanding of UV degradation and stabilization,[122,130]
- measurement of nitroxyl radical concentration,[131,132]
- plasticizer diffusion and distribution,[133]

The methods of measurement are standard techniques which permit determination of paramagnetic species. In some studies, HCl evolution was measured directly in ESR tube in addition to ESR studies.[134] The usefulness of this method in PVC degradation studies is only third to FTIR.

10.5.4 FOURIER TRANSFORM INFRARED, FTIR

Polyene index, carboxyl index, characteristic group evaluation, and degradation depth profiling are some of the most important utilities in PVC degradation studies for which FTIR data are indispensable. Rather than to show a list of different application which would be too numerous to be practical, assignment of various absorption bands is given below (Table 10.2).

Table 10.2. Assignment of absorption bands in PVC compounds.

Wavenumber, cm^{-1}	Description	Reference
3665	carboxylic acid –OH stretching	135
3200-3600	hydroxyl	135
3080-3700	hydroxyl	7
2970.8-2807.8	four bands of HCl absorption in gas-phase FTIR	158
2800-3600	hydroxyl	136
2730	aldehyde, C–H stretching	135

Table 10.2. Assignment of absorption bands in PVC compounds.

Wavenumber, cm^{-1}	Description	Reference
2220-2230	CO_2 – volatile product of UV irradiation	71
1780-1785	carbonyl of –COCl group	64,136,137
1740-1750	isolated carbonyl group (–CHCl–CO–CHCl–)	64,136,137
1737	acrylic impact modifier	138
1734	carbonyl	139
1733	carbonyl	135
1715-1720	carbonyl of –COOH group	64,136,137
1720	carbonyl	140
1700-1750	carbonyl of surface soiling agent	141
1650	polyene sequence	142,156
1630	$CaCl_2$	143
1606	cadmium octoate	144
1605	carbonyl conjugated with polyene	136
1600	polyene	139
1567	barium octoate + cadmium octoate (1:1)	144
1554	CdCl–carboxylate	145
1550	calcium stearate	146
1547	barium octoate	144
1543, 1588, 1622	zinc octoate	144
1540, 1580	metal stearates	147
1539	zinc stearate	146
1538-1545	metal lanolin fatty acids	157
1510, 1566	zinc stearate	144
1504	barium stearate	144
1450, 875	$CaCO_3$	143
1430, 1242	C–H	139
1240	epoxy group	159
1150	$CaSO_4$	143
962	C–C	139
875	–C=C– stretching	148
823	epoxy group	159
692	C–Cl stretching in atactic configuration	149
685, 614	C–Cl	139
640	C–Cl stretching in syndiotactic diad	150
637, 1427	crystalline bands	151

Table 10.2. Assignment of absorption bands in PVC compounds.

Wavenumber, cm^{-1}	Description	Reference
635	C–Cl stretching in syndiotactic configuration	149
635, 604, 1427	crystalline bands	152
616, 1435	amorphous bands	151
615, 1435	amorphous bands	152

The majority of measurements are made using KBr pellets but thick samples are measured with specular reflectance,[153] and samples with damaged surface (e.g., UV exposed samples) by either photoacoustical[154] or micro-attenuated total reflectance.[155] In some studies, microscopic attachment is also used.[143]

10.5.5 LASER PHOTOPYROELECTRIC EFFECT SPECTROMETRY

The photopyroelectric measurement technique is a valuable tool for the nondestructive evaluation of thin polymer films. The nondestructive character of the technique permits long-term studies to be performed on the same sample of slowly evolving processes such as natural weathering.[160,161] The laser mirage effect, a method of photothermal beam deflection, measures heat conduction from the surface of an optically heated sample into an adjacent fluid medium.[160] Depth profiling measurements are carried out by the technique of impulse laser photopyroelectric effect spectrometry. The measurements use an optically inhomogeneous sample, irradiated by a short optical pulse, which gives rise to a heat flux profile in the material that follows the optical absorption profile.[161]

10.5.6 MASS, MS

Mass spectroscopy is seldom used alone. In the range of analyzed publications, it was used only once to confirm chemical composition of a plasticizer.[162] Hyphenated analytical techniques use mass spectrometer as detector. TG-MS is the most common combination which was used to compare volatile degradation products of PVC and post-chlorinated PVC (post-chlorinated PVC has lower emission of benzene and toluene).[82] TG-GC-MS was used to analyze volatile products of cable compound degradation.[75,163,164] TG-MS was used in thermostability studies of PVC/PANI blends,[165] and pyrolysis-GC-MS in studies of chlorinated PVC[166] its stabilization and its blends with PVC.[171]

Identification of compounds separated by gas chromatography is another use of MS in hyphenated technique – GC-MS. It was used to identify low molecular weight plasticizers,[167] additives present in medical tubing,[168] and combination of acids in metal carboxylate stabilizers.[169]

Micro-liquid chromatography-electrospray-ion trap mass spectrometry, μ-LC-ES-ITMS, is a suitable method for analysis of tin stabilizers leaching from water pipes.[170]

10.5.7 MOSSBAUER

Mossbauer spectroscopy has been used in studies of thermal degradation of PVC stabilized with tins stabilizers.[134,172-175] It was possible to follow the stabilization process with several stabilizers.[173,174] Isomeric shift of organotin chloride was found to correspond to

its Lewis acidity.[134] In UV degradation studies it was found that the technique was insensitive and erroneous conclusions have been easily drawn.[172]

10.5.8 NEAR INFRARED, NIR

The following frequencies were assigned for some PVC groups in near and mid infrared:[176]

CH_2 symmetrical stretch	2909 cm^{-1}
CH_2 asymmetrical stretch	2931 cm^{-1}
CH_2 stretch	5829, 8544, 11104 cm^{-1}
CH stretch	2974, 5725, 8374, 10929 cm^{-1}

NIR is excellent tool in quality control of PVC products. It was used to predict color with very good results because both NIR and color determination measure changes caused by formation of polyenes.[177] In the pharmaceutical industry, blister film was controlled for color and thickness.[178] Type and concentration of plasticizer can be conveniently predicted by NIR.[179] Morphological properties of suspension PVC can be effectively monitored by NIR.[180,181]

10.5.9 NUCLEAR MAGNETIC RESONANCE, NMR

The main application of NMR studies has been historically related o long branches, products of phenolysis reaction, and end-group analysis. Starnes *et al*.[182-184] gave a detailed description of NMR spectroscopy potential, and Abbas[185] made measurements using Starnes' method. Caraculacu[53] and Hjertberg[187] applied NMR for determination of phenol incorporated in the place of labile chlorine, while Hjertberg was also successful in the identification of terminal groups in the PVC chain by using this technique. Wirth[188] described the more unusual application of NMR to study the interaction of different organotin chlorides. Ando[189] applied ^{1}H-NMR in conformation studies of meso and racemic diads in PVC.

Starnes *et al.,*[182-184] who experimented with various reducing agents, made excellent use of the full capabilities of this method by utilizing Bu_3SnD as a reducing moiety. Monodeuteration of ^{13}C atom converts its proton-decoupled NMR signal from a singlet into a triplet, due to which this signal and those from neighboring carbon undergo upfield shifts. Based on these observations, one is able to identify the original locations at which chlorine was bound. Since the structure of the chain backbone can be studied from the same measurement, the structure of the original polymer can therefore be deduced from the data collected according to Starnes' method.

Today NMR is even more prominent in PVC degradation studies. The list of the most essential applications of NMR spectroscopy is very long, and it includes:

- determination of structural defects,[190-198]
- high-field proton NMR is considered to be the only reliable technique of determination of internal and terminal double bonds in PVC,[193]
- determination of stereochemical microstructure,[199-205]
- ^{13}C NMR measurement of tacticity,[207-212]
- ^{1}H NMR measurement of tacticity,[213]

- good correlation between chemical shift and configurational sequence distribution,[214]
- branch structure,[215,216]
- branch length and chain branching (peak assignment of partially reduced PVC),[217]
- study of PVC crystallinity by solid state deuterium NMR,[218,219]
- configuration of PVC in crystallites,[220]
- model studies of PVC degradation,[221]
- Diels-Alder reaction studies,[222]
- effect of microstructure on nucleophilic substitution,[202,223]
- determination of stability of conjugated bonds in air,[224]
- PVC modification by reaction with thiols,[225,226]
- studies of structural changes caused by UV degradation,[217]
- mechanism of phosphite action by ^{31}P NMR,[221]
- studies of tin stabilizers by ^{1}H and ^{13}C NMR,[172]
- studies of tin stabilizers by ^{119}Sn NMR,[173]
- measurement of relaxation parameters by NMR MOUSE (MObile Universal Surface Explorer) and its application in weathering study of PVC coating directly on the ferromagnetic iron sheet,[227]
- studies of PVC molecular mobility by variable contact time experiment,[228]
- visualization of solvent diffusion by NMR microscopy with radio-frequency field gradients,[229]
- pulse-gradient spin-echo NMR application for studies of self-diffusion of plasticizers,[229]
- use of solid state NMR to study PVC-plasticizer interaction,[12,230]
- evaluation of crystalline structures of antioxidants and phosphites as well as distribution of these stabilizers,[170]
- studies of structure of lead stabilizers,[231,232]
- studies of principles of dielectric behavior of PVC,[198]
- reasons behind the influence of tacticity on glass transition temperature,[211]
- determination of heterogeneity of gel by pulsed NMR,[233]
- application of ^{13}C cross-polarization magic-angle-spinning depolar-decoupling NMR in studies of miscibility and phase behavior of PVC blends with other polymers,[234]
- quantification of electron-withdrawing character of solvents.[130,134]
- oil formation during mild thermooxidative degradation of PVC[235]

The above long list shows potential applications of NMR, which have made a very important contribution to the correct understanding of PVC degradation and stabilization. Together with FTIR, NMR is the most popular method used in the PVC degradation studies.

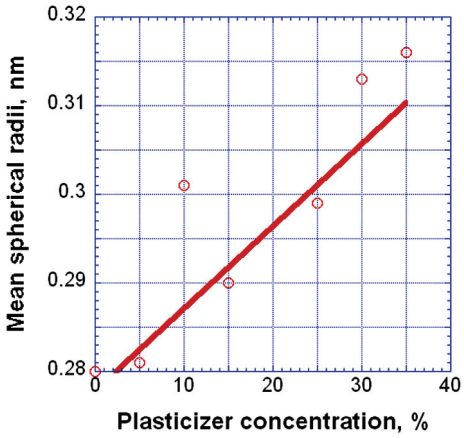

Figure 10.10. Mean spherical radii of spherical wells vs. concentration of dibutyl phthalate. [Data from Wang, C. L.; Wang, S. J., *J. Phys.: Condensed Matter*, **6**, 19, 3593-8, 1994.]

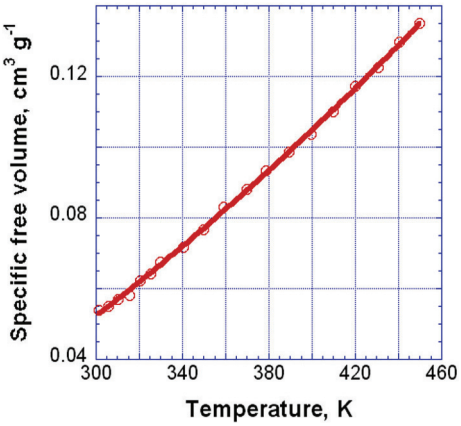

Figure 10.11. Specific free volume vs. temperature. [Data from Dlubek, G.; Bondarenko, V.; Pionteck, J.; Supej, M.; Wutzler, A.; Krause-Rehberg, R., *Polymer*, **44**, 6, 1921-1926, 2003.]

10.5.10 POSITRON ANNIHILATION LIFETIME SPECTROSCOPY, PAS

Positron lifetime depends on microstructure of polymer, namely the concentration and average size of free volume holes. Figure 10.10 shows that free volume size increases with plasticizer concentration increasing.[240] The molecules of the plasticizer dissolve into the chains of PVC and they make its free volume larger.[236] It causes the creation of the free space regions of low electron density. In those regions positrons might be formed and they may live there much longer than in the non-plasticized PVC.[236]

Figure 10.11 shows that increase in temperature contributes to increase of a free volume.[237-239]

These two observations are essential findings from measurements of positron annihilation lifetime spectroscopy. The hole volume at 100K was estimated to be 0.07 nm^3.[237] It increases above glass transition temperature from 0.10 to 0.18 nm^3.[237]

The positronium is preferentially localized and annihilated in the free-volume holes of the amorphous region; therefore, PAS is able to detect sensitively the properties of atomic-scale free-volume holes in polymers.[240] Studies of stress relaxation of PVC films which were previously stretched show that the relaxations of the free-volume size and concentration in PVC span a period of about 90 h.[240]

The changes in free-volume parameters on e-beam and microwave irradiations of PVC/SAN blends show improved interaction between the blend constituents as a result of crosslinking through hydrogen bond formation.[241]

10.5.11 RAMAN

Raman spectroscopy contributes valuable results in several areas, including:

- determination of polyenes,[63,137,198,242-245]
- orientation,[246,247]
- crystallinity and configuration,[248,248]
- depth profiling,[250-255]
- miscibility and interaction.[256,257]

The resonance Raman effect is used for the benefit of determination of polyene length. The resonance occurs if the energy of the incident light approaches that of an electronic transition. Because of the resonance the intensity of the Raman bands can be enhanced by up to a factor of 10^6, which changes a weak response to a high intensity of Raman bands, resulting in a very low detection limit of polyene.[242] For polyenes, the excitation wavelength of the optimum resonance effect depends on the length of the polyene as follows:

$$\lambda = 700 - 537.7\exp[-0.0768n] \qquad [10.4]$$

where:

λ	excitation energy in nm,
n	number of conjugated double bonds in polyene.

This equation shows that excitation with radiation of a certain wavelength probes polyene of a corresponding length. The position of vibration band recorded on Raman spectrum also depends on the polyene length according to the following equation:

$$\nu_2 = 1461 + 151.2\exp[-0.07808n] \qquad [10.5]$$

where:

ν_2 intense band of $-(CH=CH)_n-$ due to stretching vibrations, typically around 1500 cm^{-1}.

The number of polyenes was calculated from the ratio of the intensities of the C=C vibration band around 1500cm^{-1} and the C–H vibration band at 1440 cm^{-1}.[63] Formation of polyenes can be monitored by *in-situ* measurements, using the device shown in Figure 10.6.[63]

Unfortunately, Raman intensity depends on the square of the polarizability and this, in turn, on polyene lengths.[198] In the absence of accurate polarizability data, concentrations of polyenes cannot be calculated, so qualitative ratios between Raman intensities of polyenes and an internal standard are used.[198]

Raman studies show long conjugated sequences of double bonds even at very low conversion (0.01%).[137] In studies of degradation of stretched PVC films at 110°C, polyenes having up to 30 double bonds were found.[243]

Conventional Raman instruments most frequently use laser excitation having a wavelength of 514.5 or 633 nm. In near infrared, Fourier transform spectroscopy excitation wavelength of 1064 nm is used. This gives it an advantage over conventional sources because radiation in near infrared does not excite fluorescence emission which interferes with measurements.[244] Two strong bands are usually used in analysis of conjugation. These bands shift slightly depending on source but they are usually in the range of 1107 to

1128 cm^{-1} for single carbon-carbon bond and from 1488 to 1521 cm^{-1} for double carbon-carbon bonds. Raman peaks of C–Cl bond vibrations are proportional to the concentration of various triads. The following bands can be assigned to triads having different conformations:

syndiotactic triads	608, 630, 636 cm^{-1}
heterotactic triads	646, 688, 707 cm^{-1}
isotactic triads	697 cm^{-1}

Plasticizers present in formulation have also characteristic bands. For example, pure DOP is measured at 1731 cm^{-1}.[257] If DOP interacts with PVC its carbonyl double bond stretching vibration is observed around 1725cm^{-1}.[257]

Polarized resonance Raman is frequently used in the studies of molecular orientation.[7] Polarization ratio increases with draw ratio increasing.[230] In profiling studies a confocal Raman microscope is used.[250-252]

Effect of hydrotalcite on formation of polyenes during PVC thermal degradation was analyzed by Raman spectroscopy.[258]

10.5.12 TIME-OF-FLIGHT SECONDARY ION MASS SPECTROMETRY, TOF-SIMS

TOF-SIMS is used infrequently in PVC studies; in the majority of cases, to determine surface morphology of polymers or polymer blends.[259-263] TOF-SIMS helped to establish reasons for low quality of welds by analyzing compositional content of polymers on the weld interface.[259] Lateral imaging and depth profiling was used to determine surface morphology of PVC/PMMA blends.[260,262] It was found that a blend's surface was enriched with PMMA (this may be useful in design of outdoor products which will be protected by a thin layer of a durable polymer rather than UV stabilizers).[262] Surface composition of PCL and PVC blends was studied by TOF-SIMS and atomic force microscopy.[261] It was possible to show that blend is surface segregated with ridges occupied by PCL and valleys by PVC.[261]

Peaks on positive and negative ion spectra of PVC and other chlorine-containing polymers have been identified.[263]

Also, secondary ion mass spectrometry, SIMS, was used in PVC membranes to determine the presence of metal cations to which SIMS is very sensitive.[264]

10.5.13 X-RAY ANALYSIS

10.5.13.1 Small angle x-ray scattering, SAXS

Because PVC is a semi-crystalline material with low crystallinity, it is difficult to study it by x-ray analysis, therefore only infrequent contributions are published on the subject.[12,14,265-268] The crystallite size was estimated to be 6.5 nm[12] or in the range from 4 to 6.5 nm.[265] The same range was also determined for semi-crystalline intervals.[265] The microstructure of stretched films was described as an ensemble of quasi-spherical particles one-dimensionally ordered and with large distance fluctuations in the equatorial plane. The superstructure is described as fibrilar or nematic-like.[14] Fringed micelle crystal forms were suggested based on SAXS data.[267] It was concluded that annealing above the glass transition temperature enhances crystalline structure.[266] SAXS was also used to assess the effect of surface modification of PVC on its microstructure.

10.5.13.2 Wide angle x-ray scattering, WAXS or WAXD

Crystallinity can be determined by WAXS.[267,269-271] The calculation of crystallinity values based on WAXD curves is subject to three conditions: the sample should have no orientation or else an averaging factor must be applied to the intensity data; on subtracting the non-crystalline component from the WAXD profile, the resulting crystalline curve must conform to some identifiable unit cell; and the potential presence of a mesomorphous phase implies that there may be no unique non-crystalline profile applicable to all PVC WAXD curves.[271] The paper[271] contains essential remarks regarding interpretation of WAXS data. It is common to accept that crystallinity of PVC is in the range of 5 to 10%.[267]

Interpretation of WAXS patterns of PVC seems to confirm that the crystalline phase has an orthorhombic cell formed by syndiotactic chains in the planar zig-zag configuration.[272] PVC is composed of "pseudo crystals" which differ widely in perfection and size, causing a wide melting range.[219,273] It was found that sample stretching does not modify WAXS peaks.[274,275]

The degree of crystallinity increases with temperature of polymerization increasing and any thermal treatment during processing modifies crystallinity.[273]

10.5.13.3 Wide-angle neutron diffraction, WAND

Crystalline order of molded and then bi-axially stretched foils prepared from atactic PVC resin was investigated by means of wide-angle neutron diffraction.[276] According to this data, the PVC structure has low thermodynamic stability (as known from practice).

10.5.14 X-RAY PHOTOELECTRON SPECTROSCOPY, XPS

Similar to applications of TOF-SIMS, XPS is a surface analysis tool very popular in analysis of samples, including:

- exposed to UV radiation,[67,209,277,278]
- oxygen plasma treated,[279]
- argon plasma treated,[280]
- polymer blends to analyze surface distribution of component polymers,[261,262, 281]
- plasticizer migration,[282]
- distribution of adhesion promoters,[283]
- exuding stabilizers,[144]
- charring processes.[1,2]

A surface layer of about 5 nm is probed for atomic composition. In weathered samples, typical course of changes includes surface enrichment with oxygen and decline in concentration of carbon and chlorine.[67,209] If samples contain titanium dioxide, the surface undergoes even more extensive changes which can be assessed based on data in Figure 5.31.[277,278] Exposure to oxygen plasma[279] and argon plasma[280] produces even faster changes of surface composition but similar in nature to UV exposure.

Qualitative and quantitative analysis of polymer distribution on the surface of polymer blends is successfully accomplished by means of XPS analysis.[261,262,281] The results are frequently surprising. For example, only 17% PCL is found on the surface of the PCL/PVC blends even though the may contain 90% PCL.[261] Surface enrichment with PMMA

was observed in PVC/PMMA blends.[262] XPS data for blends were compared with FTIR data.[281] Surface sampling was done on the same spots and results of composition showed very good correlation, which improves expected results because FTIR excels in identification, while XPS determines concentration.

Excellent results can be obtained in analysis of the fate of additives. For example, the surface of PVC medical tubing is dominated by plasticizer;[282] it is possible to assess whether aminosilane (adhesion promoter) migrates to the interface where it expected to improve adhesion;[283] it is possible to identify that inferior adhesion of pigment to PVC film is caused by migration to the surface of Ba/Cd stabilizer;[144] or to follow the effect of additives on charring behavior of PVC.[1,2]

XPS, similar to some other methods of analysis, suffers from the fact that its soft x-ray radiation is degrading to many materials, including PVC. Figure 7.17 shows this effect and Section 7.10 contains explanations.[118,284-286]

The composition and morphology of nickel-plated PVC foils were characterized by scanning electron microscopy and X-ray photoelectron spectroscopy.[287] A compact and continuous Ni–P layer with amorphous nickel phase is formed on the PVC surface.[287]

Industrial PVC samples have been flame-treated to improve their surface adhesion.[288] Angle resolved X-ray photoelectron spectroscopy (limited X-ray damage) was used to assess the effect of the flame treatment.[288] The results showed that the chloride species appear to segregate to deeper layers than the immediate surface.[288]

10.5.15 UV-VISIBLE

UV-visible spectrophotometry is one of the most prominent methods in PVC thermal degradation studies because polyenes formed in the process of degradation selectively absorb in this range and their wavelength of absorption depends on the length of conjugated double bond sequence.

Two forms of sample are used for UV-visible spectra determination, i.e., solution or film. PVC solution used for these studies is usually prepared in tetrahydrofuran in concentrations from 0.75 to 4 g per liter.[56,186,289-291] Other authors,[292-296] used 2-4 g/l PVC solutions in hexamethylphosphortriamide and a 7% PVC solution in methylene chloride.[297] The solution method has two important limitations. First, in the course of PVC degradation, samples become less soluble and part of the polymer is lost to determination; secondly, the solvent may play an essential role in the degradation process if degradation occurs in the presence of solvent and oxygen.[198]

Studies of UV-visible spectrum with a sample in the form of film are also common. The film is prepared by casting from THF solution, obtained by a method similar to production method, or a sample is obtained from PVC material microtomed to 20 μm thin slices.[244] PVC, before heat treatment, does not absorb in UV range but after heat treatment there is a measurable absorption in the range of 280-420 nm (polyenes having 4 to 8 double bonds), and this may become part of sample preparation if it is done by heating.[72]

The major application of UV-vis spectroscopy is in UV degradation studies and determination of polyene formation (analysis of long, short, total, and distribution of polyenes).[137,299]

Two methods compete for this application: Raman and UV-vis spectrophotometry with each having advantages and disadvantages (for Raman spectroscopy evaluation see Section 10.5.11). In the case of UV-vis two methods can be used: transmission and reflection.[177] Transmission measurements are prone to easy saturation effects, especially for relatively thick commercial samples. Individual polyene sequences appear as small bands on a featureless broad background.[177] In reflectance measurements, using an integrating sphere,[136] the depth of penetration into the sample limits the ability of full characterization.[177] Sensitivity to long polyenes is generally low in the case of UV-vis spectroscopy.[300] Raman spectroscopy gives also better results in the case of determination of polyene distribution.[301] In comparative studies of both UV methods and Raman spectroscopy, it was found that Raman spectroscopy gave similar results to reflection UV-vis spectroscopy but different than that obtained from transmission studies.[63] There is no clear explanation on what might have caused the difference. It is speculated that it was either sample preparation or sample geometry (reflectance UV and Raman were using powder samples of PVC; and transmission UV films).[63]

The thermal stability of the polyvinyl chloride (PVC) filled with hydrotalcite was studied using UV-visible spectrophotometry.[302] PVC without hydrotalcite had relatively high content of the conjugated double bonds with the chain length of about 3–5. PVC with hydrotalcide had higher the content of the conjugated double bond with the chain length of about 7.[302]

The dienophilic zinc and calcium salts of 11-maleimidoundecanoic acid stabilizers were synthesized and used in PVC.[303] UV-visible spectroscopic data show that stabilizers slow down color change of PVC.[303]

10.6 CHROMATOGRAPHIC METHODS

10.6.1 GAS CHROMATOGRAPHY

Gas chromatography is frequently used in PVC studies but seldom alone. The following applications were found:

- epoxidized soybean oil,[304]
- aromatic and chlorinated hydrocarbons emitted from thermally degraded material,[305]
- CO_2 evolution from photooxidative degradation of PVC in the presence of TiO_2,[306]
- indoor pollution by alkylphenols,[307]
- HCl from thermally degraded PVC.[308]
- products of hydrothermal carbonization of PVC[328]

Inverted gas chromatography is also used to study:

- polymer-filler interaction,[324]
- plasticizer compatibility,[309]
- compatibility between PVC and nitrile rubber.[310]
- the dispersive
- component of the surface free energy and surface acid–base constants of montmorillonite/PVC[329]

- effect interactions between poly(hydroxypropyl acrylate) functional groups and the structures formed during the thermal degradation of PVC on PVC thermal stabilization[330]

In all other cases, hyphenated methods are used in which GC is used for separation of compounds in various mixtures. GC was used for the following purposes:

- pyrolysis-GC (pyrolysis at Curie point of 500°C) to study volatiles composition,[82]
- pyrolysis-GC-MS – gases from thermal decomposition,[311]
- GC-MS is used for many purposes, such as
  - volatile species formed during UV-irradiation,[312]
  - dioxins in exhaust gas from incinerator,[313]
  - vinyl chloride in water from water pipe,[17,314]
  - low molecular weight plasticizers,[167]
  - plasticizers in food and medical use,[77,315-319]
  - plasticizer indoor emissions from wallpaper and flooring,[320]
  - residual contents of plasticizers in wastes in landfills,[321]
  - guide to identification of plasticizers can be found elsewhere,[322]
  - additives in gaskets of lids for glass jars,[323]
  - organotins in edible oils,[115]
  - derivatized organotins by reaction with Grignard reagent or reduction to organotin hydrate,[325,326]
  - dibutyltin in wine by solid-phase microextraction GC-MS.[327]
  - Pyrolysis of wood-PVC mixtures[331]

10.6.2 LIQUID CHROMATOGRAPHY

High pressure liquid chromatography, HPLC, is mostly used in evaluation of low molecular weight compounds added to PVC, as follows:

- rapid determination of di-2-ethylhexyl phthalate,[332]
- quantification of plasticizers[351]
- leaching of plasticizers from dialyzers,[333,334]
- migration of plasticizer to saliva from PVC products chewed by volunteers,[335]
- anionic species formed during PVC degradation analyzed with use of ionic conductivity detector,[336]
- stabilizer concentration in PVC,[337]
- phenol concentration in PVC,[338]
- reverse-phase HPLC use for determination of plasticizer hydrophobicity.[339]

Gel permeation chromatography, GPC, is used to determine molecular weight and its distribution.[209,340-343] UV degradation is frequently followed by monitoring molecular weight changes.[336-346] Electric cables used for a long time were analyzed for molecular weight distribution and its change.[8] Effect of crosslinking was probed by GPC.[99] In order to determine depth profile of molecular weight change, PVC samples were microtomed to 20 μm slices used for molecular weight determination.[347] SEC most frequently uses a Viscotek detector which is refractometer/viscometer.

Size (steric) exclusion chromatography, SEC, is also used for molecular weight determination.[348,349] But also to separate plasticizers[65] from PVC and determine dimerization of didecylphthalate.[350] SEC uses a set of microstyrogel columns and UV and refractometer detectors.

In the case of both GPC and SEC, narrow molecular weight distribution polystyrene standards are used for calibration. This and problems with dissolution of some samples which contain insoluble gels is the most frequent reason for error.

10.7 MECHANICAL PROPERTIES

Mechanical property testing methods used in degradation studies do not differ from product testing for any other purposes. In fact, very frequently methods are selected for testing the influence of degradative processes because they are essential for characterizing product performance. Below are some examples of methods which were used for testing of various products:

- cables: shore A, tensile strength, elongation,[353]
- coatings, laminates, multilayer products: peel strength,[283]
- foams: tension and compression tests, shear stress-strain behavior, compression and torsion testing, tension and torsion testing of samples having different geometries,[354]
- geomembranes: break strength, elongation, secant modulus, tear resistance, bonded seam shear strength, hydrostatic resistance, dimensional stability,[355]
- injection molded parts and extruded profiles: tensile creep compliance,[356-358]
- profiles (window, door, other): Vickers microhardness, tensile impact, dart drop impact, Charpy impact strength,[154,359,360]
- pipes: tubular tests with compression, tension, torque, internal and external pressure, and fracture toughness.[361,362]

The additive influence under the test also has an impact on selection of the testing method, for example, the following methods were selected to assess the impact of:

- fillers: flexural modulus by three-point bending,[363,364]
- impact modifiers: impact strength, toughness, plastic deformation, fracture yield stress, tensile stress and modulus,[365]
- plasticizers: tensile strength, elongation, 100% modulus, shore D hardness, low temperature flexibility, brittleness, surface tack,[366-368]
- thermal stabilizers: tensile strength[371]

Impact testing is very frequently used in evaluation of weathered samples. Various methods of impact testing include: Izod, Gardner variable height, Dynatup drop weight.[9] Using drop weight impact testing, various formulations were compared using optical micrographs which show the effect of impact testing on ductile, semi-ductile, semi-brittle, and brittle PVC materials.[369]

There are many examples which show that weathering affects mechanical properties of materials.[122] In similar developments, the crosslinking and chain scission occurring during dehydrochlorination cause rapid changes of brittleness, tensile strength, and elongation.[128] Improvement of stabilization of recyclate increases impact strength to the

required level.[370] Examples are numerous and the above referenced sources show good practices in the application of mechanical testing methods to studies of various modes of degradation of PVC materials.

10.8 OTHER ESSENTIAL METHODS OF TESTING

10.8.1 ACTION SPECTRUM

Action spectrum is the rate of change of physical property plotted against wavelength of radiation. It shows the wavelength sensitivity. The procedure involves exposure of the samples to the narrow wavelength bands of radiation followed by measurement of the property change (most frequently color change). The light exposure can be best performed using monochromatic radiation from a spectrograph (e.g., the Okazaki Large Spectrograph Facility (NIBB) in Okazaki, Japan).[11] The spectrograph used[11] was equipped with a 30 kW xenon short-arc water-cooled lamp. Radiation was filtered through a distilled water filter to exclude heat and dispersed into a spectrum using a double-blazed plane grating with 1200 lines/mm.[11] Monochromatic radiation of the desired wavelength was obtained by placing the samples at an appropriate position on a 10-meter long focal curve.[11] A set of sharp cut-off filters was used to minimize the multiply diffracted light and other stray light reaching the sample position.[11]

In another study, samples were exposed in Weather-Ometer under filters. A set of 17 cut-off filters having the wavelength range of 266-473 nm (10% transmission) was also used.[5] Filter pairs were used to define the relative effects of narrow bands of the source radiation.[5]

In the above two experiments, yellowness index was a property being measured but any other property may be selected, bearing in mind that various changes require different amounts of energy to cause measurable change (gloss change is faster than color change but color change is faster than tensile strength changes).

10.8.2 COULTER COUNTER

Particle size distribution of PVC grades is an essential parameter in material processing and degradation studies. Particle size distribution and size averages are determined by particle counting in a Coulter counter (e.g., Multisizer 3). It provides number, volume, mass, and surface area size distributions in one measurement, with an overall sizing range of 0.4 μm to 1,200 μm. Its response is unaffected by particle color, shape, composition or refractive index. Samples of 20 mg of resin were contained in 250 mL of electrolyte consisting of 1% solution of NaCl (in double distilled water), and three drops of ethanol as dispersant. Calibration is performed with standard size particles.

10.8.3 GEL CONTENT

Gel is formed because of crosslinking reactions by various crosslinkers and caused by mechanisms of degradation. In gel content determination, the samples are Soxhlet extracted for 20 h with tetrahydrofuran, and the residue is dried for 12 h at 80°C and weighed[372] (or in vacuum oven at 60°C for 20 h).[373] The amount of gel is expressed as the percentage of the total amount of material which can form the gel.[372] Gel content was studied in samples exposed to UV radiation. Samples containing TiO_2 did not contain gel,

unlike samples without TiO_2 which had gel content correlating with the length of exposure.[374]

10.8.4 OZONOLYSIS

The number of internal double bonds (or sequences) is determined by following the changes in M_n caused by oxidative cleavage by ozone of all double bonds.[375] 0.5 g PVC is dissolved in 100 ml cyclohexanone and a small amount of methanol is added to facilitate the cleavage of the ozonide formed.[375] The ozonolysis is performed at -20°C for 2 h and the polymer is recovered by precipitation in methanol and drying in vacuum for 24 h.[375] The number of internal cleavages per 1000 monomer units, $(C=C)_n/1000$ VC) is calculated from the number-average molecular weight before (M_{n0}) and after (M_n) the oxidative treatment, as follows:[375]

$$(C=C)_n/1000 \text{ VC} = 62{,}500(1/M_n - 1/M_{n0}) \qquad [10.6]$$

10.8.5 PEROXIDE TITRATION

Peroxides can be determined by iodometric titration as follows: 0.5 g PVC is swollen in 75 cm^3 of deaerated CHCl, for 12 h. Deaerated glacial acetic acid (1 cm^3) is added followed by 25 cm^3 of freshly prepared 5% NaI. After standing for 4 h in the dark at room temperature, the liberated I is titrated with 0.1N $Na_2S_2O_3$.[131]

Two types of titration were carried out by Gaumet and Gardette.[376] The first method was based on the reduction of hydroperoxides by ferrous ions in solution and the second on reduction by gaseous sulfur dioxide.[376] The first method gives accurate results of hydroperoxides concentrations, but it is not suitable for the titration of hydroperoxides in thermally oxidized PVC, since the preliminary swelling of the samples does not occur even after long immersion in appropriate solvents (dichloromethane, hexafluoroisopropanol).[376]

10.8.6 RHEOLOGICAL STUDIES

Rheological studies of PVC formulations are necessary elements of technology development in almost any kind of PVC application. Particle size distribution affects plastisol behavior. Rheometrics mechanical spectrometer with parallel disks was used to study PVC plastisol to understand effect of particle size distribution, paste aging, the effect of shear rate on plastisol viscosity.[377] A controlled stress rheometer with a cylindrical sensor can also be used for this type of studies.[378]

Fusion and gelation have an important influence on rheological properties of PVC formulation. Measuring rheological properties, a parallel plate in oscillatory measurements below the processing temperatures shows that the more fused the samples, the more elastic the response. When measuring above the highest processing temperature, the response is completely opposite, i.e., the more gelated the samples, the more viscous behavior is observed.[388]

A qualitative model satisfactorily explains the rheological behavior of PVC plastisols during gelation and fusion.[341] Fast gelation is observed when plasticizer has a good solvent power and/or when PVC resin has large number of fine particles or low molecular weight.[373] Addition of recycled polymer markedly increases viscosity of plastisol.[379]

Capillary rheometry was used to study formulation variables such as lubricant, impact modifier, and process aid on their influence of process conditions and results.[380]

The control of the thermal degradation rate of rigid PVC is very critical in extrusion. A quantitative method of measuring the true degradation rate of PVC (including influence of rheological properties) is proposed for formulating rigid vinyl compounds.[381] The data for this model come from measurements using a Kayeness capillary rheometer.[381] The study shows a very good correlation between the capillary rheometer data and the extrusion melt temperature, melt viscosity, and the rate of degradation of PVC.[381]

Components of formulation affect rheological properties. Plasticizer type and concentration have a very strong influence on rheological properties of compounded PVC.[382] Brabender rheology tests were run to compare changes in the fusion characteristics of formulations having different lubricants.[383] Combination of a lubricating system and thermal stabilizer was studied by Brabender plastograph and capillary rheometry to determine the most efficient composition.[384] Capillary rheometry was also useful to balance the effect of mass temperature and screw speed on the fusion level and mechanical properties of a rigid PVC pipe.[385] Capillary rheometry was used to monitor PVC thermal and shear stress degradations separately.[386] Based on capillary rheometer tests, stabilizers can be efficiently optimized to reduce both degradation processes.[386]

Thermal aging and crosslinking processes can be effectively followed by mechanical spectroscopy.[387] The above examples show that rheological studies are not only essential in technology and process development but their results are very important for PVC degradation studies because mechanical energy can directly (mechanodegradation) and indirectly (mechanical energy conversion to heat) cause degradation.

10.9 INTERNATIONAL STANDARDS

The list of international standards related to PVC has more than 1000 entries. Here, only the most relevant standards to PVC degradation and its testing are included for countries which are known to lead standardization efforts.

AS 2369.2-1993	Materials for solar collectors for swimming pool heating - Flexible or plasticized polyvinyl chloride
AS/NZS 1462.15:1996	Methods of test for PVC pipes and fittings - Method for determination of vinyl chloride monomer content
AS/NZS 1462.19:2006	Methods of test for plastics pipes and fittings - C-ring test for fracture toughness of PVC pipes
AS/NZS 1660.2.3:1998	Test methods for electric cables, cords and conductors - Insulation, extruded semi-conductive screens and non-metallic sheaths - Methods specific to PVC and halogen free thermoplastic materials
ASTM D256-10	Standard Test Methods for Determining the Izod Pendulum Impact Resistance of Plastics
ASTM D638-10	Standard Test Method for Tensile Properties of Plastics
ASTM D1004-13	Standard Test Method for Tear Resistance (Graves Tear) of Plastic Film and Sheeting
ASTM D1203-10	Standard Test Methods for Volatile Loss From Plastics Using Activated Carbon Methods
ASTM D1243-14	Standard Test Method for Dilute Solution Viscosity of Vinyl Chloride Polymers
ASTM D1435-13	Standard Practice for Outdoor Weathering of Plastics
ASTM D1499-13	Standard Practice for Filtered Open-Flame Carbon-Arc Exposures of Plastics

ASTM D1525-09	Standard Test Method for Vicat Softening Temperature of Plastics
ASTM D1708-13	Standard Test Method for Tensile Properties of Plastics by Use of Microtensile
ASTM D1709-09	Standard Test Methods for Impact Resistance of Plastic Film by the Free-Falling Dart Method
ASTM D1755-09	Standard Specification for Poly(Vinyl Chloride) Resins
ASTM D1921-12	Standard Test Methods for Particle Size (Sieve Analysis) of Plastic Materials
ASTM D1929-13a	Standard Test Method for Determining Ignition Temperature of Plastics
ASTM D2115-10	Standard Practice for Oven Heat Stability of Poly(Vinyl Chloride) Compositions
ASTM D2124-99(2011)	Standard Test Method for Analysis of Components in Poly(Vinyl Chloride) Compounds Using an Infrared Spectrophotometric Technique
ASTM D2152-13	Standard Test Method for Adequacy of Fusion of Extruded Poly(Vinyl Chloride) (PVC) Pipe and Molded Fittings by Acetone Immersion
ASTM D2222-14	Standard Test Method for Methanol Extract of Vinyl Chloride Resins
ASTM D2288-97(2001)	Standard Test Method for Weight Loss of Plasticizers on Heating - withdrawn
ASTM D2383-14	Standard Practice for Testing Plasticizer Compatibility in Poly(Vinyl Chloride) (PVC) Compounds Under Humid Conditions
ASTM D2396-94(2012)	Standard Test Methods for Powder-Mix Time of Poly(Vinyl Chloride) (PVC) Resins Using a Torque Rheometer
ASTM D2457-13	Standard Test Method for Specular Gloss of Plastic Films and Solid Plastics
ASTM D2538-02(2010)	Standard Practice for Fusion of Poly(Vinyl Chloride) (PVC) Compounds Using a Torque Rheometer
ASTM D2565-99(2008)	Standard Practice for Xenon Arc Exposure of Plastics Intended for Outdoor Applications
ASTM D2843-10	Standard Test Method for Density of Smoke from the Burning or Decomposition of Plastics
ASTM D2863-13	Standard Test Method for Measuring the Minimum Oxygen Concentration to Support Candle-Like Combustion of Plastics (Oxygen Index)
ASTM D3030-11	Standard Test Method for Volatile Matter (Including Water) of Vinyl Chloride Resins
ASTM D3045-92(2010)	Standard Practice for Heat Aging of Plastics Without Load
ASTM D3291-11	Standard Practice for Compatibility of Plasticizers in Poly(Vinyl Chloride) Plastics Under Compression
ASTM D3364-99(2011)	Standard Test Method for Flow Rates for Poly(Vinyl Chloride) with Molecular Structural Implications
ASTM D3367-13	Standard Test Method for Plasticizer Sorption of Poly(Vinyl Chloride) Resins Under Applied Centrifugal Force
ASTM D3418-12e1	Standard Test Method for Transition Temperatures of Polymers By Differential Scanning Calorimetry
ASTM D3465-14	Standard Test Method for Purity of Monomeric Plasticizers by Gas Chromatography
ASTM D3591-97(2011)	Standard Test Method for Determining Logarithmic Viscosity Number of Poly(Vinyl Chloride) (PVC) in Formulated Compounds
ASTM D3596-14	Standard Practice for Determination of Gels (Fisheyes) In General-Purpose Poly(Vinyl Chloride) (PVC) Resins
ASTM D3678-14	Standard Specification for Rigid Poly(Vinyl Chloride) (PVC) Interior-Profile Extrusions
ASTM D3679-13	Standard Specification for Rigid Poly(Vinyl Chloride) (PVC) Siding
ASTM D3749-13	Standard Test Method for Residual Vinyl Chloride Monomer in Poly(Vinyl Chloride) Resins by Gas Chromatographic Headspace Technique
ASTM D3801-10	Standard Test Method for Measuring the Comparative Burning Characteristics of Solid Plastics in a Vertical Position
ASTM D3814-06	Standard Guide for Locating Combustion Test Methods for Polymeric Materials - withdrawn
ASTM D3835-02	Standard Test Method for Determination of Properties of Polymeric Materials by Means of a Capillary Rheometer
ASTM D3915-06	Standard Specification for Rigid Poly(Vinyl Chloride) (PVC) and Chlorinated Poly(Vinyl Chloride) (CPVC) Compounds for Plastic Pipe and Fittings Used

	in Pressure Applications
ASTM D4005-92(2010)	Standard Test Method for Plastic-Coated Fabrics - Completeness of Fusion of PVC Dispersion Coatings
ASTM D4092-07(2013)	Standard Terminology: Plastics: Dynamic Mechanical Properties
ASTM D4216-13	Standard Specification for Rigid Poly(Vinyl Chloride) (PVC) and Related PVC and Chlorinated Poly(Vinyl Chloride) (CPVC) Building Products Compounds
ASTM D4226-11	Standard Test Methods for Impact Resistance of Rigid Poly(Vinyl Chloride) (PVC) Building Products
ASTM D4272-14	Standard Test Method for Total Energy Impact of Plastic Films By Dart Drop
ASTM D4329-13	Standard Practice for Fluorescent UV Exposure of Plastics
ASTM D4364-13	Standard Practice for Performing Outdoor Accelerated Weathering Tests of Plastics Using Concentrated Sunlight
ASTM D4440-08	Standard Test Method for Plastics: Dynamic Mechanical Properties: Melt Rheology
ASTM D4459-12	Standard Practice for Xenon-Arc Exposure of Plastics Intended for Indoor Applications
ASTM D4495-12	Standard Test Method for Impact Resistance of Poly(Vinyl Chloride) (PVC) Rigid Profiles by Means of a Falling Weight
ASTM D4508-10	Standard Test Method for Chip Impact Strength of Plastics
ASTM D4526-12	Standard Practice for Determination of Volatiles in Polymers by Static Headspace Gas Chromatography
ASTM D4551-12	Standard Specification for Poly(Vinyl Chloride) (PVC) Plastic Flexible Concealed Water-Containment Membrane
ASTM D4674-02a(2010)	Standard Practice for Accelerated Testing for Color Stability of Plastics Exposed to Indoor Office Environments
ASTM D4703-10a	Standard Practice for Compression Molding Thermoplastic Materials into Test Specimens, Plaques, or Sheets
ASTM D4726-09	Standard Specification for Rigid Poly(Vinyl Chloride) (PVC) Exterior-Profile Extrusions Used for Assembled Windows and Doors
ASTM D4803-10	Standard Test Method for Predicting Heat Buildup in PVC Building Products
ASTM D5023-07	Standard Test Method for Plastics: Dynamic Mechanical Properties: In Flexure (Three-Point Bending)
ASTM D5024-07	Standard Test Method for Plastics: Dynamic Mechanical Properties: In Compression
ASTM D5025-12	Standard Specification for Laboratory Burner Used for Small-Scale Burning Tests on Plastic Materials
ASTM D5026-06(2014)e1	Standard Test Method for Plastics: Dynamic Mechanical Properties: In Tension
ASTM D5208-14	Standard Practice for Fluorescent Ultraviolet (UV) Exposure of Photodegradable Plastics
ASTM D5225-14	Standard Test Method for Measuring Solution Viscosity of Polymers with a Differential Viscometer
ASTM D5260-04(2010)	Standard Classification for Chemical Resistance of Poly(Vinyl Chloride) (PVC) Homopolymer and Copolymer Compounds and Chlorinated Poly(Vinyl Chloride) (CPVC) Compounds
ASTM D5507-99(2012)	Standard Test Method for Determination of Trace Organic Impurities in Monomer Grade Vinyl Chloride by Capillary Column/Multidimensional Gas Chromatography
ASTM D5630-13	Standard Test Method for Ash Content in Plastics
ASTM D5991-09	Standard Practice for Separation and Identification of Poly(Vinyl Chloride) (PVC) Contamination in Poly(Ethylene Terephthalate) (PET) Flake
ASTM D6110-10	Standard Test Method for Determining the Charpy Impact Resistance of Notched Specimens of Plastics
ASTM D6263-11	Standard Specification for Extruded Rods and Bars Made From Rigid Poly(Vinyl Chloride) (PVC) and Chlorinated Poly(Vinyl Chloride) (CPVC)
ASTM D6360-07	Standard Practice for Enclosed Carbon-Arc Exposures of Plastics
ASTM D6864-11	Standard Specification for Color and Appearance Retention of Solid Colored Plastic Siding Products

ASTM D7083-04(2010)e1	Standard Practice for Determination of Monomeric Plasticizers in Poly(Vinyl Chloride) (PVC) by Gas Chromatography
ASTM D7309-13	Standard Test Method for Determining Flammability Characteristics of Plastics and Other Solid Materials Using Microscale Combustion Calorimetry
ASTM F1057-10	Standard Practice for Estimating the Quality of Extruded Poly (Vinyl Chloride) (PVC) Pipe by the Heat Reversion Technique
BS 7412:2007	Specification for windows and doorsets made from unplasticized polyvinyl chloride (PVC-U) extruded hollow profiles
BS EN 15346:2007	Plastics. Recycled plastics. Characterization of poly(vinyl chloride) (PVC) recyclates
BS EN 50414:2006	Test methods for analysis of lead in PVC taken from insulation and sheath of electric and optical fibre cables. Method A: Total lead content determination with flame excitation atomic absorption spectrometry. Method B: Qualitative analysis of lead by lead sulphide staining
BS EN 50497:2007	Recommended test method for assessment of the risk of plasticizer exudation from PVC insulated and sheathed cables
BS EN 60811-3-2:1995, IEC 60811-3-2:1985	Insulating and sheathing materials of electric cables. Common test methods. Methods specific to PVC compounds. Loss of mass test. Thermal stability test
DIN 16830-1	High impact polyvinyl chloride (PVC-HI) window profiles; testing
DIN 53381-1	Testing of plastics; determination of thermostability of polyvinyl chloride (PVC); dehydrochlorination methods
DIN 53408	Testing of Plastics; Determination of Solubility Temperature of Polyvinyl Chloride (PVC) in Plasticizers
DIN 53743	Testing of plastics; gas chromatographic determination of vinyl chloride (VC) in polyvinyl chloride (PVC)
DIN 54800	Testing of plastics; preparation of polyvinyl chloride (PVC) pastes for testing purposes
DIN EN 477	Unplasticized polyvinylchloride (PVC-U) profiles for the fabrication of windows and doors - Determination of the resistance to impact of main profiles by falling mass
DIN EN 478	Unplasticized polyvinylchloride (PVC-U) profiles for the fabrication of windows and doors - Determination of appearance after exposure at 150°C
DIN EN 479	Unplasticized polyvinylchloride (PVC-U) profiles for the fabrication of windows and doors - Determination of heat reversion
DIN EN 513	Unplasticized polyvinylchloride (PVC-U) profiles for the fabrication of windows and doors - Determination of the resistance to artificial weathering; German version EN 513:1999
DIN EN 12608	Unplasticized polyvinylchloride (PVC-U) profiles for the fabrication of windows and doors - Classification, requirements and test methods; German version EN 12608:2003
DIN EN 13900-2	Pigments and extenders - Methods of dispersion and assessment of dispersibility in plastics - Part 2: Determination of colouristic properties and ease of dispersion in plasticized polyvinyl chloride by two-roll milling DIN
DIN EN 71-5	Safety of toys - Part 5: Chemical toys (sets) other than experimental sets
DIN EN ISO 305	Plastics - Determination of thermal stability of poly(vinyl chloride), related chlorine-containing homopolymers and copolymers and their compounds - Discoloration method (ISO 305:1990); German version EN ISO 305:1999
GB/T 11793.2-1989	Technical requirements on mechanical and weathering properties for PVC windows
GB/T 11793.3-1989	Testing methods on mechanical and weathering properties for PVC windows
GB/T 12004.2-1996	PVC paste resins--Preparation of a paste
GB/T 16613-1996	Preparation of polyvinyl chloride (PVC) pastes for test purposes--Dissolver method
GB/T 2951.7-1997	Common test methods for insulating and sheathing materials of electric cables Part 3: Methods specific to PVC compounds. Section two: Loss of mass test. Thermal stability test
IEC 60189-1 ED. 3.0 EN:2007	Low-frequency cables and wires with PVC insulation and PVC sheath - Part 1: General test and measuring methods

ISO 176:2005	Plastics -- Determination of loss of plasticizers -- Activated carbon method
ISO 177:1988	Plastics -- Determination of migration of plasticizers
ISO 178:2010	Plastics -- Determination of flexural properties
ISO 179-1:2010	Plastics -- Determination of Charpy impact properties -- Part 1: Non-instrumented impact test
ISO 179-2:1997	Plastics -- Determination of Charpy impact properties -- Part 2: Instrumented impact test
ISO 180:2000	Plastics -- Determination of Izod impact strength
ISO 182-1:1990	Plastics - Determination of the tendency of compounds and products based on vinyl chloride homopolymers and copolymers to evolve hydrogen chloride and any other acidic products at elevated temperatures - Part 1: Congo red method
ISO 182-2:1990	Plastics - Determination of the tendency of compounds and products based on vinyl chloride homopolymers and copolymers to evolve hydrogen chloride and any other acidic products at elevated temperatures - Part 2: pH method
ISO 182-3:1993	Plastics - Determination of the tendency of compounds and products based on vinyl chloride homopolymers and copolymers to evolve hydrogen chloride and any other acidic products at elevated temperatures - Part 3: Conductometric method
ISO 182-4:1993	Plastics - Determination of the tendency of compounds and products based on vinyl chloride homopolymers and copolymers to evolve hydrogen chloride and any other acidic products at elevated temperatures - Part 4: Potentiometric method
ISO 458-2:1985	Plastics -- Determination of stiffness in torsion of flexible materials -- Part 2: Application to plasticized compounds of homopolymers and copolymers of vinyl chloride
ISO 527-1:2012	Plastics -- Determination of tensile properties -- Part 1: General principles
ISO 604:2002	Plastics -- Determination of compressive properties
ISO 868:2003	Plastics and ebonite -- Determination of indentation hardness by means of a durometer (Shore hardness)
ISO 877-1:2009	Plastics -- Methods of exposure to solar radiation -- Part 1: General guidance
ISO 877-2:2009	Plastics -- Methods of exposure to solar radiation -- Part 2: Direct weathering and exposure behind window glass
ISO 877-3:2009	Plastics -- Methods of exposure to solar radiation -- Part 3: Intensified weathering using concentrated solar radiation
ISO 899-1:2003	Plastics -- Determination of creep behaviour -- Part 1: Tensile creep
ISO 899-2:2003	Plastics -- Determination of creep behaviour -- Part 2: Flexural creep by three-point loading
ISO 974:2000	Plastics -- Determination of the brittleness temperature by impact
ISO 1060-2:1998	Plastics - Homopolymer and copolymer resins of vinyl chloride - Part 2: Preparation of test samples and determination of properties
ISO 1419:1995	Rubber- or plastics-coated fabrics -- Accelerated-ageing tests
ISO 1628-2:1998	Plastics - Determination of the viscosity of polymers in dilute solution using capillary viscometers - Part 2: Poly(vinyl chloride) resins
ISO 2039-1:2001	Plastics -- Determination of hardness -- Part 1: Ball indentation method
ISO 2039-2:1987	Plastics -- Determination of hardness -- Part 2: Rockwell hardness
ISO 2578:1993	Plastics -- Determination of time-temperature limits after prolonged exposure to heat
ISO 3114:1977	Unplasticized polyvinyl chloride (PVC) pipes for potable water supply - Extractability of lead and tin - Test method
ISO 4574:1978	Plastics - PVC resins for general use - Determination of hot plasticizer absorption
ISO 4582:2007	Plastics -- Determination of changes in colour and variations in properties after exposure to daylight under glass, natural weathering or laboratory light sources
ISO 4608:1998	Plastics - Homopolymer and copolymer resins of vinyl chloride for general use - Determination of plasticizer absorption at room temperature
ISO 4612:1999	Plastics - Preparation of PVC pastes for test purposes - Planetary-mixer method
ISO 4892-1:1999	Plastics -- Methods of exposure to laboratory light sources -- Part 1: General

	guidance
ISO 4892-2:2013	Plastics -- Methods of exposure to laboratory light sources -- Part 2: Xenon-arc lamps
ISO 4892-3:2013	Plastics -- Methods of exposure to laboratory light sources -- Part 3: Fluorescent UV lamps
ISO 4892-4:2013	Plastics -- Methods of exposure to laboratory light sources -- Part 4: Open-flame carbon-arc lamps
ISO 6259-2:1997	Thermoplastics pipes -- Determination of tensile properties -- Part 2: Pipes made of unplasticized poly(vinyl chloride) (PVC-U), chlorinated poly(vinyl chloride) (PVC-C) and high-impact poly(vinyl chloride) (PVC-HI)
ISO 6383-2:1983	Plastics - Film and sheeting - Determination of tear resistance - Part 2: Elmendorf method
ISO 6451:1982	Plastics coated fabrics -- Polyvinyl chloride coatings -- Rapid method for checking fusion
ISO 6721-1:2011	Plastics -- Determination of dynamic mechanical properties -- Part 1: General principles
ISO 6721-2:2008	Plastics -- Determination of dynamic mechanical properties -- Part 2: Torsion-pendulum method
ISO 9370:2009	Plastics -- Instrumental determination of radiant exposure in weathering tests -- General guidance and basic test method
ISO 11468:1997	Plastics - Preparation of PVC pastes for test purposes - Dissolver method
ISO 11673:2005	Unplasticized poly(vinyl chloride) (PVC-U) pressure pipes - Determination of the fracture toughness properties
ISO 18373-1:2007	Rigid PVC pipes - Differential scanning calorimetry (DSC) method - Part 1: Measurement of the processing temperature
ISO 29664:2010	Plastics -- Artificial weathering including acidic deposition
JIS K 6720-1:1999	Plastics -- Homopolymer and copolymer resins of vinyl chloride (PVC) -- Part 1: Designation system and basis for specifications
JIS K 6720-2:1999	Plastics -- Homopolymer and copolymer resins of vinyl chloride -- Part 2: Preparation of test samples and determination of properties
JIS K 6723:1995	Plasticized polyvinyl chloride compounds
JIS K 7110:1999	Plastics -- Determination of Izod impact strength
JIS K 7111-1:2012	Plastics -- Determination of Charpy impact properties -- Part 1: Non-instrumented impact test
JIS K 7111-2:2006	Plastics -- Determination of Charpy impact properties -- Part 2: Instrumented impact test
JIS K 7115:1999	Plastics -- Determination of creep behaviour -- Part 1: Tensile creep
JIS K 7116:1999	Plastics -- Determination of creep behaviour -- Part 2: Flexural creep by three-point loading
JIS K 7118:1995	General rules for testing fatigue of rigid plastics
JIS K 7119:1972	Testing method of flexural fatigue of rigid plastics by plane bending
JIS K 7120:1987	Testing methods of plastics by thermogravimetry
JIS K 7121:1987	Testing methods for transition temperatures of plastics
JIS K 7124-1:1999	Plastics film and sheeting -- Determination of impact resistance by the free-falling dart method -- Part 1: Staircase methods
JIS K 7124-2:1999	Plastics film and sheeting -- Determination of impact resistance by the free-falling dart method -- Part 2: Instrumented puncture test
JIS K 7128-1:1998	Plastics -- Film and sheeting -- Determination of tear resistance -- Part 1: Trouser tear method
JIS K 7128-2:1998	Plastics -- Film and sheeting -- Determination of tear resistance -- Part 2: Elmendorf tear method
JIS K 7128-3:1998	Plastics -- Film and sheeting -- Determination of tear resistance -- Part 3: Right angled tear method
JIS K 7171:2008	Plastics -- Determination of flexural properties
JIS K 7181:2011	Plastics -- Determination of compressive properties
JIS K 7201-1:1999	Plastics -- Determination of burning behaviour by oxygen index -- Part 1: Guidance
JIS K 7201-2:2007	Plastics -- Determination of burning behaviour by oxygen index -- Part 2:

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JIS K 7211-1:2006	Plastics -- Determination of puncture impact behaviour of rigid plastics -- Part 1: Non-instrumented impact testing
JIS K 7211-2:2006	Plastics -- Determination of puncture impact behaviour of rigid plastics -- Part 2: Instrumented impact testing
JIS K 7212:1999	Plastics -- Determination of thermal stability of thermoplastics -- Oven method
JIS K 7215:1986	Testing methods for durometer hardness of plastics
JIS K 7216:1980	Testing method for brittleness temperature of plastics
JIS K 7217:1983	Analytical method for determining gases evolved from burning plastics
JIS K 7219-1:2011	Plastics -- Methods of exposure to solar radiation -- Part 1: General guidance
JIS K 7219-2:2011	Plastics -- Methods of exposure to solar radiation -- Part 2: Direct weathering and exposure behind window glass
JIS K 7226:1998	Plastics -- Determination of time-temperature limits after prolonged exposure to heat
JIS K 7229:1995	Determination of chlorine in chlorine-containing polymers, copolymers and their compounds
JIS K 7350-2:2008	Plastics -- Methods of exposure to laboratory light sources Part 2: Xenon-arc sources
JIS K 7350-3:2008	Plastics -- Methods of exposure to laboratory light sources -- Part 3: Fluorescent UV lamps
JIS K 7350-4:2008	Plastics -- Methods of exposure to laboratory light sources -- Part 4: Open-flame carbon-arc lamps
JIS K 7362:1999	Plastics -- Determination of changes in colour and variations in properties after exposure to daylight under glass, natural weathering or laboratory light sources
JIS K 7363:1999	Plastics -- Instrumental determination of radiant exposure in weathering tests -- General guidance and basic test method
JIS K 7373:2006	Plastics -- Determination of yellowness index and change of yellowness index
JIS K 7380-1:2011	Plastics -- Homopolymer and copolymer resins of vinyl chloride -- Determination of residual vinyl chloride monomer -- Part 1: Gas-chromatographic method
JIS K 7380-2:2011	Plastics -- Homopolymer and copolymer resins of vinyl chloride -- Determination of residual vinyl chloride monomer -- Part 2: Gas-chromatographic analysis of dry powder
JIS K 7382:2002	Plastics -- Homopolymer and copolymer resins of vinyl chloride -- Determination of volatile matter (including water)
JIS K 7383:2002	Plastics -- Preparation of PVC pastes for test purposes -- Dissolver method
JIS K 7384:2002	Plastics -- Preparation of PVC pastes for test purposes -- Planetary-mixer method
JIS K 7385:2002	Plastics -- Vinyl chloride homopolymers and copolymers -- Determination of chlorine content
JIS K 7386:2002	Plastics -- Homopolymer and copolymer resins of vinyl chloride for general use -- Determination of plasticizer absorption at room temperature

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11

Principles of Stabilization

11.1 FUNCTIONS OF PVC STABILIZERS

11.1.1 HYDROGEN CHLORIDE BINDING

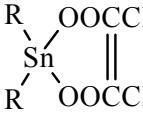
HCl acceptance is unquestionably the most important feature of any chemical substance used as a thermal stabilizer of poly(vinyl chloride). Although there is basically no need to confirm this fact, since the catalytic effect of HCl is commonly accepted, many efforts have been made in order to study this phenomenon. The following set of chemical reactions shows the extent of the process:

metal soaps:

$$M(OOCR)_2 + HCl \longrightarrow ClMOOCR + RCOOH$$
$$ClMOOCR + HCl \longrightarrow MCl_2 + RCOOH$$

organotins:

(i) $R_2Sn(OOCR')_2 + HCl \longrightarrow R_2Sn(Cl)OOCR' + R'COOH$
$R_2Sn(Cl)OOCR' + HCl \longrightarrow R_2SnCl_2 + R'COOH$

(ii) 
$+ HCl \longrightarrow R_2Sn(Cl)OOCCH=CHCOOH$
$R_2Sn(Cl)OOCCH=CHCOOH + HCl \longrightarrow R_2SnCl_2 + (CHCOOH)_2$

(iii) $R_2Sn(SR")_2 + HCl \longrightarrow R_2Sn(Cl)SR" + R"SH$
$R_2Sn(Cl)SR" + HCl \longrightarrow R_2SnCl_2 + R"SH$

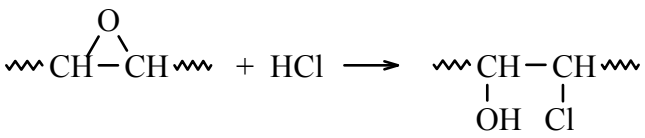
where:

R	aliphatic group (mainly: methyl, butyl and octyl),
R'	carboxylic acid rest (mainly lauric or monoisooctyl maleate),
R"	mainly isooctyl thioglycollate, isooctyl thiopropionate, thiododecane.

phosphites:

$$(RO)_3P + HCl \longrightarrow (RO)_2PHO + RCl$$
$$(RO)_2PHO + HCl \longrightarrow ROP(OH)HO + RCl$$
$$ROP(OH)HO + HCl \longrightarrow H_3PO_3 + RCl$$

epoxidized compounds:



The reaction schemes suggest that some of these reactions proceed in stages, but the naturally-observed phenomenon seems to be of a rather more complicated nature. It is known from Michel's earlier works[1,2] with white lead that the process of HCl reaction goes through intermediate stages. These studies, repeated by Ball[3] for lead carbonate with careful analysis of reaction products by X-ray diffraction, proved without any doubt that lead chloride was the only product of reaction with HCl which formed no intermediate.

Similar studies for metal soaps are still in progress, and suggestions so far presented are even more controversial. The question to be answered in this case is: What is the order in which the reactions proceed? Two options are possible. Either HCl reacts first (the more probable option) with the stabilizer in its initial form $[M(OOR)]_2$, producing, first M(Cl)OOR (which would suggest that the initial form is more reactive towards HCl than the partially reacted product). Or partially reacted stabilizer is so reactive that a second act of HCl acceptance immediately follows the first one. Many authors[4-10] observed in their studies that the first possibility is most likely correct. This author[11] studied the kinetics of reaction of HCl with various metal stearates in alcoholic solutions, and kinetic data suggested two different reaction rates, which should normally be regarded as confirming the first option. The results were interpreted in an earlier work[12] according to the same assumption.

All above suggestions were made, however, without the most essential proof, i.e., isolation of chloro-metal carboxylate. Later, studies for both hydrolysis and synthesis of metal stearates of Ca, Ba, Zn and Cd in various media helped to isolate and analyze intermediate compounds.[13] In water no compound other than normal metal stearate was detected, and therefore, studies were repeated in alcoholic solution. Results, as confirmed by IR spectra and elementary analysis, were exactly the same. The conclusion, therefore, was that probably the polar character of solvent does not allow one to obtain the intermediate product, whose change in symmetry is a destabilizing factor in such a media. The studies were repeated in water-free acetone, and intermediates were found for Ba and Ca stearates but not for Cd and Zn.

To further confirm these observations, another experiment was planned in which PVC and calcium stearate samples were sealed in extreme ends of the same glass tube, and the side containing PVC inserted into an oven so as to form HCl, which can be reacted by the thermal stabilizer. Several such tubes, processed under the same conditions, were kept for varying times to achieve varying conversions of calcium stearate. The resulting calcium stearate was immediately analyzed by X-ray and later for the contents of Cl, which were indirectly determined by analyzing the consumption of Ag ions by AAS. Results confirmed previously-obtained data, since 81.3% of the reacted calcium stearate did not contain a trace of this product, but when alcohol was added to the sample and evaporated

again, adequate amounts of calcium stearate were recovered, which shows both the possibility of reaction between calcium stearate intermediate and its lack of stability in alcoholic solution, as was found in another experiment.

How do we interpret these observations? It is assumed for further discussion that the reactivity of Ca and Ba intermediates is lower in non-polar media than that of initial carboxylates, and thus they can be stable under normal reaction conditions (PVC thermal degradation), which is not the case with the intermediates of Zn and Cd, which react immediately with a second molecule of HCl.

Considering the participation of organotin stabilizers in reaction with HCl, one question is important. Does reaction lead finally to $SnCl_4$, or does the reaction with HCl only occur with groups other than alkyl? This question has been considered by many authors, and the overwhelming majority believe that HCl does not react with the C–Sn bond.[6,14-16] Only van Hoang[17] found for model compounds that reaction of aryl-substituted organotins may result in the formation of $SnCl_4$. Rockett[16] had explained earlier that this reaction might occur only when C–Sn bonds are cleaved due to the presence of, for example, phenyl rings. One should notice that for products of type $RSnY_3$ or R_3SnY, the final product of reaction is $RSnCl_3$ or R_3SnCl, respectively. There is still little doubt of the correctness of this conclusion, since it is known that, for example, R_2SnCl_2 retards PVC dehydrochlorination,[18] but since the phenomenon is explained by reaction other than with HCl, this mechanism will be dealt with later.

Epoxidized compounds are able to accept HCl, which is a fact confirmed by a good deal of research.[12,19-21] The case of organic phosphites is slightly more complicated, since it was discovered that only alkyl phosphites, due to their greater electron density at the center,[22] can react with HCl,[23,24] while aryl phosphite can only form complexes with HCl.[24]

From this discussion we can already observe the possibility that various forms of stabilizer reaction products with HCl may react among themselves. The studies[13] show that the following reaction takes place:

$$2ClCaOOCR \longrightarrow Ca(OOCR)_2 + CaCl_2$$

when alcohol was added to the Ca stearate, 81.3% of which was reacted with HCl. Possibilities for a reaction of this type were mentioned in so many papers[7-9,25-28] (although without proof, as found elsewhere[13]) that there is little doubt that this is a true mechanism of PVC stabilization. Vymazal *et al.*[31] suggested that ClCdOOCR can be isolated (an unlikely possibility, since this compound was found to be unstable).

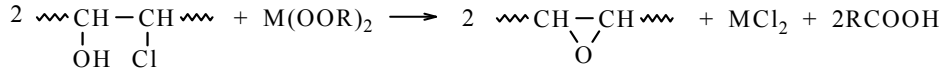
The peculiarity of exchange reaction is that the metal type also plays an essential role here, which causes the following reactions to take place:

$$ZnCl_2 + Ca(OOCR)_2 \longrightarrow Zn(OOCR)_2 + CaCl_2$$
$$CdCl_2 + Ba(OOCR)_2 \longrightarrow Cd(OOCR)_2 + BaCl_2$$

These reactions help to recover zinc and cadmium carboxylates in their initial form. Organotins also work according to the same principle; moreover, they tend to balance their

chlorines, which is quite useful, considering that the products substituted with more chlorines appear at the end of the process, and these are usually more toxic and catalytic.[29,30]

Also, epoxidized compounds are able to interact in stabilizing compositions according to the following equation:[20]



Epoxy compound in this reaction acts as a moiety participating in HCl transportation to the stabilizer.

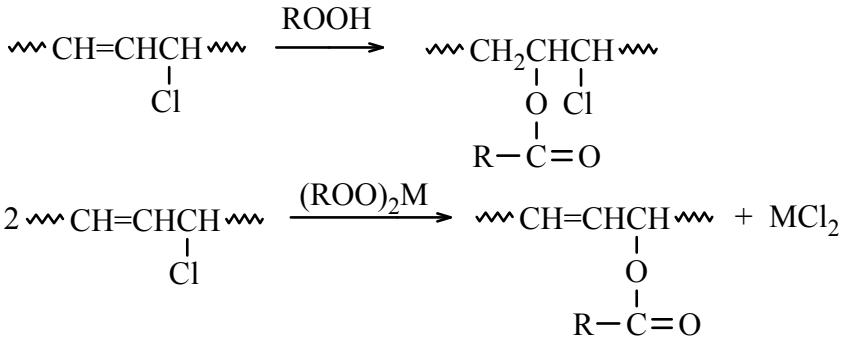
We can see that, so far, we have not encountered too many problems in explaining the experimental observations, and this image of completeness, so far as stabilizer reaction with HCl is concerned, would remain if not for the fact that we should also expect to have data on the stabilizers' reactivity with HCl. Although this subject belongs to kinetics rather than to the mechanism of stabilizer's action (for the mechanism it is also important to know the comparative data for various products which differ in chemical nature). Unfortunately, there is little knowledge on this subject. One can only find traces of information, which do not appear fully reliable.

Stabilizer's reactivity with HCl is also of interest. At the end of the induction period, a mixture stabilized by Ba/Cd stabilizer cadmium stearate was reacted in 50%, while barium stearate reacted in 80%.[31] Polymer color is changed when 80-90% of Ca/Zn or Ba/Cd stabilizer reacts with HCl.[32] The reactivity of organotins with HCl, in alcoholic solutions, was higher than that of metal soaps.[11] When organotins were reacted with a model compound resembling PVC, their reactivity was very high.[14,33] Figge[34] observed that the dehydrochlorination rate was higher when stabilizer concentration had fallen below 0.5%. The order of reactivity of organotins was thioglycolate > maleate > laurate.[35]

The reactivity of phosphites towards HCl was said to be lower than that of metal soaps.[36] Two phosphites were compared for their reactivity with HCl.[37] Tri-n-octyl phosphite was fast to react with HCl, whereas triphenyl phosphite was hardly reacting at all.[37] Triaryl phosphites cannot undergo the Arbuzov rearrangement, and thus cannot react with HCl, $ZnCl_2$, or labile PVC chlorines.[37]

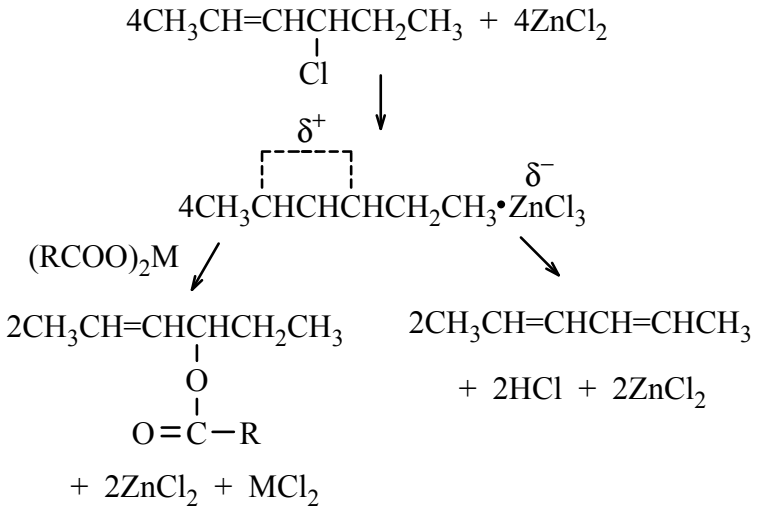
11.1.2 REMOVAL OF REACTIVE CHLORINE

The most probable offender causing PVC instability is the presence of β-chloroallyl groups, which can initiate a chain reaction of HCl elimination, leading to polyene length extension. Stabilizers are thought to be able to react with this β-chlorine atom. It should be noted from the beginning that there are two theoretical possibilities for β-chloroallylic group deactivation:



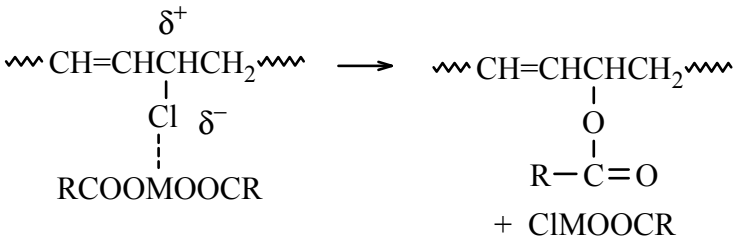
both preventing the formation of conjugated sequences. There is no clear explanation as to which of these reactions is likely to take place. The most common view since Frye's work[36-38] is that the second reaction occurs, which can be easily understood, taking into account the high reactivity of metal carboxylates with chlorine.

Guyot[24] believes that the reaction of chlorine replacement by carboxylic acid rest is catalyzed by $ZnCl_2$, which forms an intermediate according to the following equation:

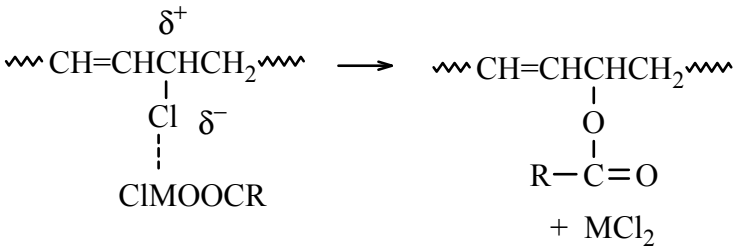


The results come from studies of low-molecular models, and suggest two possibilities for further reaction of an intermediate (substitution of acid rest in the presence of active stabilizer or otherwise polyene extension). Guyot[24] stated that replacement goes on as long as stabilizer is present, and when it is exhausted, the reaction pattern changes to rapid HCl elimination, which leads to abrupt deterioration of the sample. A similar mechanism is thought to apply to cadmium carboxylates, but this is not the case with calcium

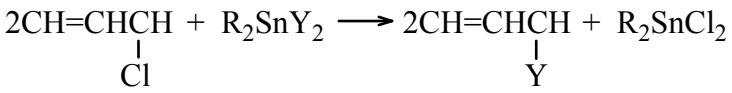
and barium carboxylates.[24] From studies by Braun,[9] the sequence of reactions would include the following stage:



From this author's studies referred to above,[13] it appears that, since the salt having formula ClMOOCR (where M = Zn or Cd) is so unstable, the above reaction should rather be seen as



This will suggest that very unstable, partially reacted stabilizer is responsible for acid rest substitution and breaking conjugation. This view is supported by some studies.[10,24,39] Similarly, organotins are able to replace chlorides:[40]



The chlorine replacement by organotin rests has been proven without a doubt by Starnes,[41] who demonstrated that PVC dehydrochlorination decreases when the amount of sulfur incorporated into the polymer chain increases. This partially confirms that sulfur linkages with carbon are more stable and not easily hydrolyzed by HCl which is evolved, and it also shows why organotins (especially sulfur-containing ones) are more efficient stabilizers than metal soaps. The method of dechlorination by reduction with Bu_3SnH is described elsewhere. This method has been used successfully to determine branches in PVC chain by ^{13}C NMR.[42-46] Also, Me_3Al[43] and dibutyl ester and butyllithium[44] were used for dechlorination. According to Adeniyi and Scott,[46] the replacement of allylic chlorine by reaction with tin carboxylate is side reaction not a primary stabilizing mechanism.

According to Starnes *et al*.[47] thiol plasticizers stabilize color by destroying labile structural defects (allylic chlorine). This prevents the initiation and growth of conjugated

polyene chromophores. The defects are either removed by reductive dechlorination or by the nucleophilic displacement of labile chlorine:

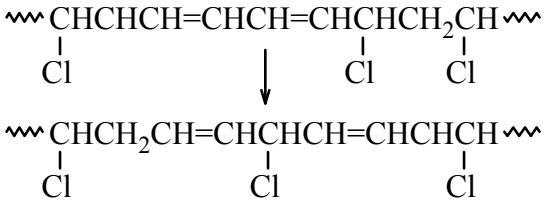
$$RCl + 2R'SH \longrightarrow RH + R'SSR' + HCl$$
$$RCl + R'SH \longrightarrow RSR' + HCl$$

Summarizing the above discussion, some metal soaps (Zn, Cd) are able to replace the β-chlorine atoms, as do organotins and phosphites.

11.1.3 REACTIONS WITH METAL CHLORIDES

Figures 11.1 and 11.2 show how the presence of various chlorides affects the PVC dehydrochlorination rate.[18]

The effect of the reaction of HCl with metal carboxylates is typical, i.e., $ZnCl_2$ and $CdCl_2$ strongly affect dehydrochlorination while the presence of other chlorides is almost irrelevant for the degradation rate. In the case of organotin chloride, one should first mention that another research group[48] obtained results which are not exactly similar to those presented in Figure 11.2, in the sense that, according to their data, the presence of trichloride increases the dehydrochlorination rate when compared with control. Wirth *et al*.[18] explain the effect of organotin chloride by its participation in an allylic rearrangement, as follows:



The newly formed structure is more stable, according to Wirth *et al*.[18] Organotin chlorides are able to stabilize PVC color, which is attributable to the allylic rearrangement.

Organic stabilizers may interact with other stabilizers' reaction products with HCl if they are present in the same reaction environment. Phosphites are thought to be able to react with zinc chloride according to the scheme below:[8,23]

$$ZnCl_2 + 2P(OR)_3 \longrightarrow (RO)_2P(O)ZnP(O)(OR)_2 + 2RCl$$

The only other known reaction of metal chlorides has been discussed in Section 11.1 with exchange of chlorine between zinc or cadmium chlorides and carboxylates of calcium and barium, respectively.

11.1.4 REACTIONS WITH ISOLATED UNSATURATIONS

Minsker[49-51] repeatedly showed that incorporation of carboxylic acid rest and its removal is in a dynamic equilibrium (substitution occurs before stabilizer is exhausted followed by high concentrations of HCl causing removal of incorporated acid rests). Guyot[24] believes that the direction of the reaction is changed when stabilizer is consumed.

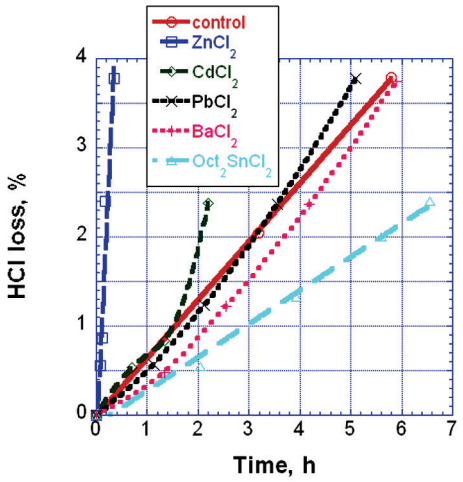


Figure 11.1. PVC thermal dehydrochlorination rate in the presence of various chlorides. [Data from Wirth, H. O.; Mueller, H. A.; Wehner, W., *J. Vinyl Technol*., **1**, 51,1979.]

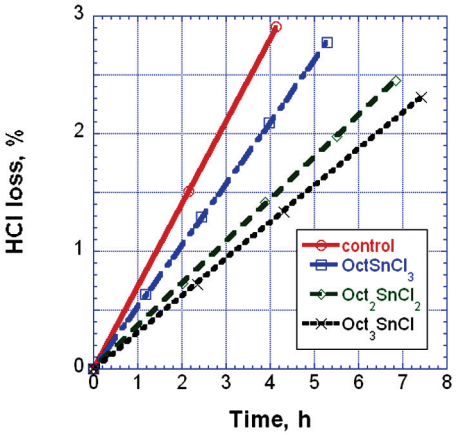


Figure 11.2. Thermal dehydrochlorination rate in the presence of various octyltin chlorides.[Data from Wirth, H. O.; Mueller, H. A.; Wehner, W., *J. Vinyl Technol*., **1**, 51,1979.]

The possibility of reaction with double bonds, which have already been formed or were available in the PVC chain, was not clearly indicated in the literature in the case of metal carboxylates, in contrast to the action of organotins[52] and phosphites,[23] which are believed to take part in the following reactions:

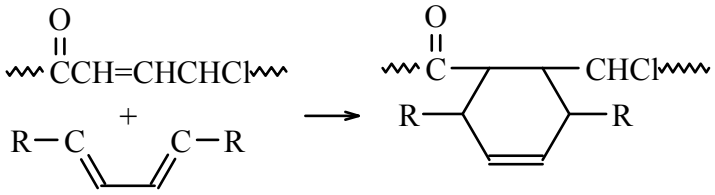
$$R_2Sn(SCH_2COOR)_2 + HCl \longrightarrow R_2Sn(Cl)SCH_2COOR + ROCOCH_2SH$$

$$ROCOCH_2SH + \sim CH_2CH{=}CH \sim \longrightarrow \sim CH_2CH_2\underset{\displaystyle SCH_2COOR}{CH} \sim$$

$$\sim \underset{\displaystyle O}{\overset{\displaystyle \|}{C}}CH{=}CH \sim + P(OR)_3 \xrightarrow{+HCl} \sim \underset{\displaystyle O}{\overset{\displaystyle \|}{C}}CH_2\underset{\displaystyle O{=}P(OR)_2}{CH} \sim + RCl$$

The reaction of thiols with double bonds was confirmed by measuring the unsaturations in PVC during treatment time; similarly, the reaction of phosphites was confirmed. Sulfur-free organotins were not able to react with the double bonds already present. The above reactions help to remove allylic chlorines which initiate thermal degradation.[46]

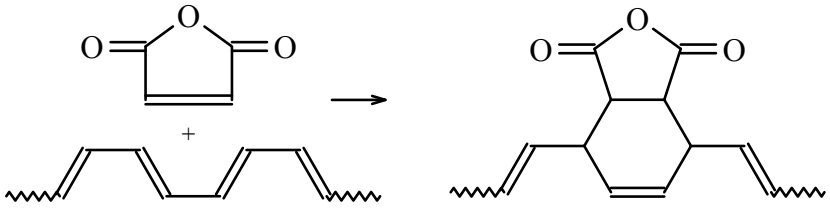
According to Minsker and Zaikov,[53] dienophilic oxyvinylene groups react with conjugated dienes according to the Diels-Alder reaction:



This reaction proceeds under mild conditions (353K) with cyclopentadiene, piperylene, isoprene, 5-methyl- 1.3.6-heptatriene, etc., and results in the removal of internal unsaturated C=C groups from PVC chains, similar to the reactions with organic phosphites.[53]

11.1.5 REACTIONS WITH CONJUGATED UNSATURATIONS

Diels-Alder addition of dienophiles to conjugated unsaturation leads to the disruption and shortening of conjugated unsaturations. The process does not stop, or even inhibit, degradation but it does improve the color of the degraded polymer:



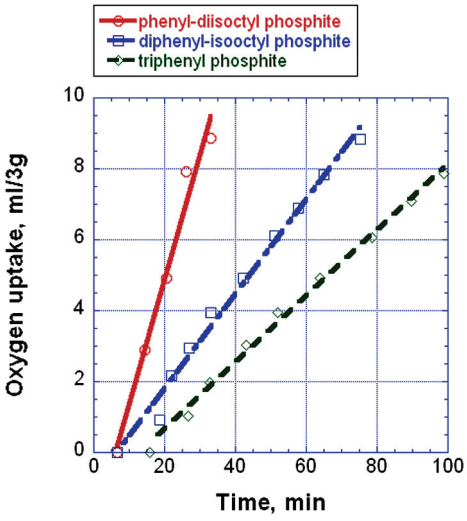


Figure 11.3. Self-oxidation stability of the phosphites. [Data from Kovacs, E.; Wolkober, Z., *J. Polym. Sci., Symp.*, **40**, 73, 1973.]

Bartholin *et al.*[54] show, in PVC samples heated in trichlorobenzene solution at 187°C in the presence of mixture of zinc and calcium stearates, the very weak carbonyl absorption, which after an initial decrease, increases as a sharp band near 1734 cm^{-1} progressively shifting towards lower wavenumbers and then decreases with simultaneous broadening. This indicates the possibility of substitution of acid rests into double bonds (authors suggest that it occurs by reaction with tertiary chlorines).[54]

11.1.6 DECOMPOSITION OF HYDROPEROXIDES

In the early years of PVC stabilization, antioxidants were added to the compositions containing metal soaps until it was found that some of them take part in photolytic reactions. The action of PVC ther-

mal stabilizers is enhanced when they are used together with phosphites. Phosphites by themselves exhibit varying resistance towards oxidative changes, as can be seen from Figure 11.3.

Phosphites reacting with hydroperoxides obey the first order reaction-rate kinetics. In the presence of oxygen they retard the rate of PVC dehydrochlorination, which is due to the termination of thermooxidative reaction chains.[23] Their reaction with peroxides is represented by the following equation:

$$R'OOH + P(OR)_3 \longrightarrow R'OH + O{=}P(OR)_3$$

These studies were more recently confirmed by Jakupca *et al*.[56] who studied oxidation of paraffins at 180°C in the presence of triphenyl and tri-n-octyl phosphites. Alkyl phosphite was more reactive towards peroxides than aryl phosphite. Tri-n-octyl phosphite was rapidly oxidized to the phosphate.[56] Triphenyl phosphite was also converted into triphenyl phosphate, but at a much slower rate compared to alkyl phosphite.[56] It should be noted that although alkyl phosphites are more reactive than aryl phosphites, they are also less hydrolytically stable.[56]

Similar processes in the presence of organotins are more complicated. There is a difference between sulfur-free and sulfur-containing organotins. Sulfur-free organotins are not able to react with peroxides below a certain level; therefore, material stabilized with them always contains certain amounts of peroxides.[57] Adeniyi and Scott[46] suggest that tin carboxylates only reduce HCl concentration, which lowers formation of hydroperoxide but they have no effect on oxidation. Burley[58] has similar observations.

The sulfur-containing organotins can reduce the level of peroxide formation almost to nil, but not at the beginning of thermooxidation, when they even seem to increase the rate of peroxide formation. Cooray[57] explains that the tin mercaptides convert hydroperoxides to tin sulfenates, which at elevated temperatures produce sulfur acids having an antioxidative action. It should be noted that sulfur-containing stabilizers are not effective photo-antioxidants because they, or their oxidation products, are photosensitizers.[46]

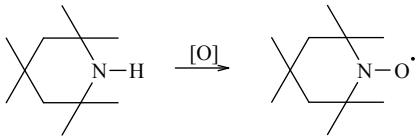
11.1.7 REMOVAL OF REACTIVE RADICALS (CHAIN-BREAKING FUNCTION)

The other important function of stabilizers is that of radical deactivation. According to Mori,[59] both metal soap and organotin stabilizers are effective in the deactivation of radicals, but organotins are more efficient than metal soaps. In the case of metal soaps, only those containing zinc and cadmium are believed to participate in a deactivation reaction by a mechanism of unknown nature. Ayrey and Poller[40,60] presented a mechanism of radical deactivation which illustrates the participation of the alkyl group in the process. A similar mechanism describing the action of organotins during thermal degradation was proposed by Gupta and St. Pierre,[61] who argued against the commonly approved view that the alkyl groups play an essential role in PVC stabilization due to reacting macroradicals formed during degradation.

Following discovery of hindered amine light stabilizers, they became the choice stabilizers to deal with radicals.

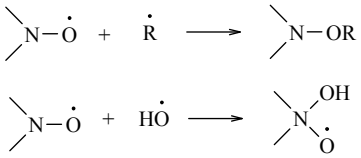
The mechanism of action of HALS differs from UV absorbers in that they are unable to absorb UV radiation. Instead, they protect materials by their ability to terminate the radicals formed. The selection of a specific HALS is determined by the properties of the system in which it must perform (pK_b). Depending on the group attached to the nitrogen atom, HALS types vary in basicity. Their basicity should be synchronized with the basicity of the material to be protected. A basic HALS should be used with a basic material and *vice versa*. Acid components in the material will interact with the basic HALS to hinder its performance. It is also essential to determine if the selected HALS is compatible with the matrix. A variety of HALS with varying solubility in different materials are available.

The single most important feature of HALS is their ability to form stable radicals always available in the materials that participate in reactions and lead to increased stability. Stable nitroxyl radicals are formed during the oxidation process:



They are stable and, under some conditions, they behave like free radicals. Their stability is very important because it means that they will not abstract hydrogen from polymer molecules – a reaction which can lead to

chain processes. At the same time, they are reactive towards free-radicals as the following reactions show:



These reactions deactivate free-radicals and contribute to the increased stability of polymers because they break the chain reaction process. ESR studies[62] show the possibility of free electron exchange between two nitroxyl groups placed in one molecule but this process does not seem to result in an increased ability to quench excited states. Mono, bi, and poly-nitroxyl compounds react with radicals at similar rates.

Further information on weathering can be found in a specialized monograph on the subject.[63]

11.1.8 UV SCREENING

Limiting the incoming radiation is a function of UV absorbers.[23-35] The Beer-Lambert law, commonly used for the quantitative evaluation of radiant energy absorption, shows that:

$$\ln(I_t/I_o) = -Ecl \qquad [11.1]$$

where:

I_t intensity of transmitted light,
I_o intensity of incident light,

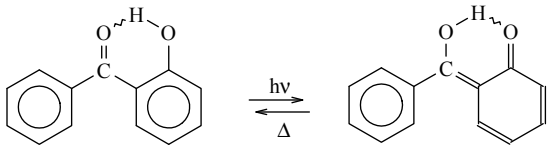
E molar absorption coefficient,
c concentration of chromophores,
l material thickness.

This implies that a material's optical properties depend on the concentration of the groups which may absorb radiation. This statement would be valid if the basic assumptions of Beer-Lambert Law are fulfilled, namely:

- incident radiation is monochromatic
- the light intensity decrease depends on absorption alone
- absorption occurs in a volume of limited cross-section and each absorbing center is independent of all others.

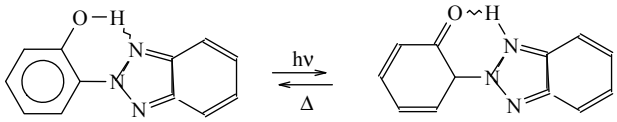
In reality, none of these assumptions are valid, so there are substantial deviations from the Beer-Lambert Law.

The mechanism of energy dissipation is essentially similar for most UV absorbers. This involves tautomeric forms that exist either in the excited or in the ground states. The tautomeric forms participate in an energy dissipation process that protects both the material and the UV stabilizer itself. 2-hydroxybenzophenones normally exist in the keto-form, then change to the enol-form as they absorb energy:

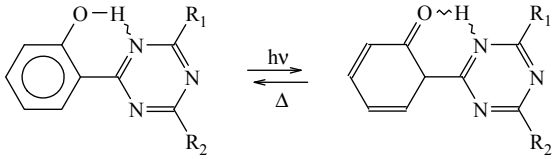


Dissipation of energy returns the UV absorber to its initial keto-form without a change in the chemical composition of the stabilizer.

Hydroxyphenylbenzotriazole absorbs light and reacts in a similar manner:



as does 2-hydroxyphenyl-S-triazine:



The common feature of these conversions is a rapid internal hydrogen transfer. The reverse reaction is exothermic. Heat produced is dissipated in the matrix. This energy dissipation can only occur if internal hydrogen bonding is possible. If there is hydrogen bonding between the UV absorber and the matrix, the energy transfer becomes disrupted, which may cause reduced efficiency of the stabilizer.

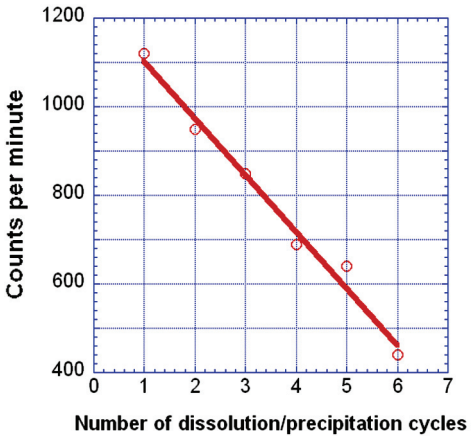


Figure 11.4. Radioactivity vs. number of dissolution/precipitation cycles for PVC containing dibutyl-1-^{14}C-tin bis(monomethyl maleate). [Data from Frye, A. H.; Horst, R. W.; Paliobagis, A. M., *J. Polym. Sci., Part A*, **2**, 1765, 1964.]

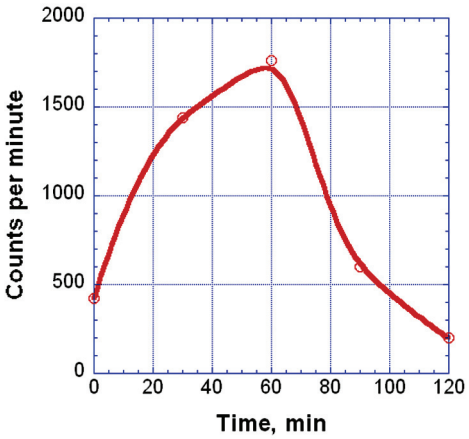


Figure 11.5. Radioactivity vs. time of heating at 175°C for PVC containing dibutyl-1-^{14}C-tin bis(monomethyl maleate). [Data from Frye, A. H.; Horst, R. W.; Paliobagis, A. M., *J. Polym. Sci., Part A*, **2**, 1765, 1964.]

Further information on weathering can be found in a specialized monograph on the subject.[63]

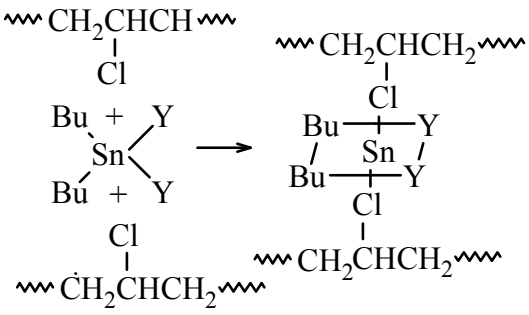
11.2 THEORIES

11.2.1 FRYE AND HORST

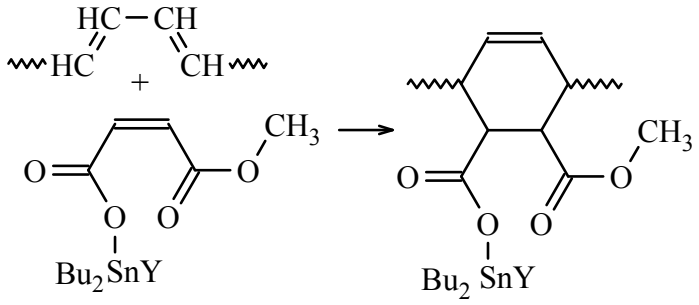
Frye and Horst[64-68] formulated the first theory of stabilization which was later reinforced by the results of Ayrey *et al*.[70-73] Frye and Horst proposed in their first two papers[64,65] (late 1950s) that acid rests are being substituted into a polymer chain in the act of replacement of labile chlorine atoms. They also stated that replacement groups are more resistant towards pyrolytic elimination than the original groups they have replaced.

In the next series of experiments (early 1960s),[66-68] they used a radiotracer technique to investigate the mechanism of action of a range of tin stabilizers. They have made two observations illustrated by Figures 11.4 and 11.5. Figure 11.4 shows that repeated dissolution and precipitation of resin milled with dibutyl-1-^{14}C-tin bis(monomethyl maleate) (a butyl proton marked with radioactive isotope)[66] had progressively decreased radioactivity, which suggested to investigators that although there was an association between stabilizer or its rest and polymer chain, the association was by means of weaker bonds than covalent bonds. Figure 11.5 shows that radioactivity increases with the time of thermal treatment but then rapidly decreases (please note that the sample at radioactivity peak at about 60 min was used in the experiment described in Figure 11.4).

The above findings influenced the perception of the mechanism proposed by Frye and Horst,[66] which suggests the following association between stabilizer and polymer:



This contradicted the mechanism proposed by Kenyon[69] published a decade earlier, based on similar experiments (radiotracer) but with dibutyltin diacetate. Kenyon also found that part of the "associated" stabilizer can be removed by dissolution/precipitation but the remainder stays attached to the polymer. It should be noted that Frye *et al*.[66] did not completely exclude the possibility of replacement of labile chlorine by a reaction involving the Y group of stabilizer. Further studies[67] revealed that similar to findings by Kenyon, radioactivity stabilizes after 12-13 cycles and this remainder has been attributed to the product of the Diels-Alder reaction, as follows:



Frye *et al*.[68] in their final paper were trying to accommodate the action of other thermal stabilizers studied, such as, for example, dibutyltin β-mercaptopropanoate, which cannot form Diels-Alder products but still leaves radioactivity after dissolution/precipitation treatment. They gave many potential schemes of reaction, with one of them being the reaction of stabilizer with peroxides by which stabilizer rest was attached to the chain with improvement of stability.

It took another 10 years before the mechanism of tin stabilizer action was affirmed by Ayrey *et al*.[70-73] based on scientific evidence also from radiotrace studies. Their mechanism is given by the following equations:[71]

$$Bu_2SnY_2 + RCl \longrightarrow Bu_2SnYCl + RY$$
$$Bu_2SnY_2 + 2RCl \longrightarrow Bu_2SnCl_2 + 2RY$$

It is difficult today to determine the reasons for the difference in results obtained by both groups but analysis of the facts shows how complicated and time consuming are the processes leading to conclusions which we now take for granted.

11.2.2 APPLICATION OF THE DEBYE-HÜCKEL THEORY

The Debye-Hückel theory provides a method to obtain activity coefficients.[74] The activity is proportional to the concentration by a factor known as the activity coefficient, which takes into account the interaction energy of ions. Levai *et al*.[75-79] applied Debye-Hückel theory to simulate stabilization progress with mixtures of metal stearates. Debye-Hückel theory is given by the following equation:[76]

$$k_e = k_e^0 10^{-m\sqrt{I}} \qquad [11.2]$$

where:

k_e		rate constant of the ionic replacement of the allylic chlorine,
k_e^0		value of k_e extrapolated to infinite dilution,
m	=	$3.65 \times 10^6/(\varepsilon T)^{2/3}$,
ε		permittivity
I	=	αx^0; ionic strength,
α		the degree of dissociation of the stabilizer system, which is defined as the ratio of the concentrations of stearate ions, x^-, and stearate groups, x^0,
x^0		initial concentration of stearate groups.

The degree of dissociation was calculated using the following relationship:

$$\alpha = 0.5 - [CO]/x^0 \qquad [11.3]$$

where:

[CO]	the equilibrium concentration of the complex given by the following equation: $(CaSt_2^0 - [CO])(ZnSt_2^0 - [CO]) = K_C[CO]$
$CaSt_2^0$, $ZnSt_2^0$	the initial concentrations of the two stearates,
K_C	equilibrium constant of complexation.

The meaning of complexation is explained by the following chemical equations:

$$CaSt_2 \longleftrightarrow CaSt^+ + St^-$$
$$ZnSt_2 \longleftrightarrow ZnSt^+ + St^-$$
$$CaSt[ZnSt_3] \longleftrightarrow Ca[ZnSt_3]^+ + St^-$$

The concentration of stearate ions can be expressed by the following equation:

$$x^- = [CaSt_2] + [ZnSt_2] + [C] \qquad [11.4]$$

where:

[C]	the concentration of complex.

because each mole of calcium stearate, zinc stearate, and the complex produce one mole of stearate ions. This means that reaction can be monitored by a sum of stearate ions.

Induction period is calculated from the following equation:

$$\tau = \frac{x^0 + (K-1)[x^0 - \log(\alpha k_e x^0 + 1)/(\alpha k_e)]}{v} \qquad [11.5]$$

where:

v	rate of dehydrochlorination
K	ratio of the rate constants of propagation and termination of polyene formation, k_2/k_1.

The above kinetic model permits us to study the influence of different dissociating abilities of mixed stearates (e.g., Zn/Ca or Cd/Ba). Ba and Ca stearates gave shorter induction periods, as was explained by their high dissociation constants as compared with Cd and Zn stearates. Complexation decreased the ionic strength and, according to the Debye-Hückel theory, increased the ionic replacement of the allylic chlorine atoms in PVC by ester groups, thereby increasing the induction times.[76] Solubility and rate of solution of the stabilizers and their reactivity with hydrogen chloride, not included in the model, were found to play an important part in the efficiency of the stabilizers.

This model assumes an ionic mechanism of stabilization which does not agree with the accepted mechanisms of PVC degradation.

11.2.3 KINETIC MODEL OF PVC STABILIZATION

In a series of papers,[80-86] Prochaska and Wypych outlined a theory of PVC stabilization and a kinetic model which allows one to calculate (predict) the induction period of PVC degradation for formulations containing single and mixed PVC stabilizers. Computer programs were developed which permit simulation of PVC degradation with use of predetermined constants without a need for further experimentation.[83-85] These programs permit simulation of results for different concentrations of one or two thermal stabilizers in a mixture as well as help explaining the exact nature of synergism of stabilizer composition.[83-85] The following information contains a short description of the theory and its applications.

This theory of stabilization relies on the use of several sets of data which are either obtained from experimental studies or calculated based on experimental data. These data include:

- induction period of degradation (time to determinable emission of HCl),
- constants of dehydrochlorination rates without stabilizer, influenced by partially reacted stabilizer(s), and influenced by fully reacted stabilizer(s) (metal chloride(s)),
- quantity of stabilizer(s) in formulation,
- reaction capacity of stabilizer with HCl (maximum amount of HCl which can be reacted by stabilizer; this value can either be calculated from stoichiometry if chemical formulation is fully known, or it can be determined by titration method[81]),
- constant of reaction rate of partially reacted stabilizer (RMeCl) with HCl.

Having these data, the program is able to calculate the following output data for any selected interval of time and the elapsed time:

- quantity of produced HCl,
- quantity of HCl reacted with first stabilizer in its initial and partially reacted form,
- quantity of HCl reacted with the second stabilizer in its initial and partially reacted form,
- quantity of stabilizers in their initial and partially reacted (RMeCl) form,
- rate of HCl reaction with each stabilizer in initial and partially reacted form,
- quantity of partially reacted stabilizer(s) and quantity of metal chlorides already formed,
- quantity of each stabilizer in the initial form,
- percents of unreacted stabilizers,
- quantity of produced HCl (bound by stabilizer and emitted).

Before calculations can be accomplished, input data must be collected. We will begin with determination of the induction period, which is a standard method discussed in details in Section 10.1.2. These methods also permit determination of constants of dehydrochlorination rates without stabilizer, constants of dehydrochlorination in the presence of reacted stabilizer(s) (metal chloride(s)).

The quantities of stabilizers in formulation are known and stabilizer's HCl reaction capacity can be either calculated for pure compounds of known composition or determined by titration with HCl in solution by any common method of titration. Table 11.1 contains HCl reaction capacity for some common stabilizers (commercial stabilizers included in the table are not produced now but were in common use when the study[81] was conducted).

Table 11.1. HCl reaction capacity of some PVC thermal stabilizers. [Data from Wypych, G., *Angew. Makromol. Chem.*, **48**, 654, 1-15, 1975.]

Stabilizer	HCl reaction capacity, mg HCl/1 g of stabilizer
Cadmium stearate	108.0
Zinc stearate	115.5
Dibasic lead phthalate	267.8
Tribasic lead sulfate	286.0
Mark 553 (organotin)	148.2
Irgastab ABC-2 (Zn/Cd=2:1)	120.0
Irgastab CZ-59 (Zn/Ca=2:1)	67.5
Nuostab V 1277 (Ba/Cd/Zn=9:6:2)	49.1

Table 11.1 shows that lead stabilizers have exceptionally large HCl reaction capacities (for this reasons they were very popular because they offered long-term stability). Commercial stabilizers have relatively low HCl capacities, especially if they are liquid, because compounds used to dissolve active compounds have no HCl reaction capacity (unless they are phosphites or epoxy compounds).

All reaction rate constants are given by the following equations:

$$v_{1i} = k_1[R_2Me]_i[HCl]_i \quad [11.6]$$

$$v_{2i} = k_2[RMeCl]_i[HCl]_i \quad [11.7]$$

$$v_{3i} = k_3[RMeCl]_i[C\text{-}Cl]_i + v_0 \quad [11.8]$$

$$v_{4i} = k_4[MeCl_2]_i[C\text{-}Cl]_i + v_0 \quad [11.9]$$

where:

$[R_2Me]_i$	concentration of stabilizer at time t_i,
$[RMeCl]_i$	concentration of partially reacted stabilizer at time t_i,
$[MeCl_2]_i$	concentration of metal chloride at time t_i,
$[HCl]_i$	concentration of HCl evolved at time t_i,
$[C\text{-}Cl]_i$	concentration of C–Cl bonds at time t_i,
$k_{1...4}$	reaction rate constants.

Because the number of C–Cl bonds does not change for practical purposes of kinetic equations, then equations [11.8] and [11.9] become simpler:

$$v_{3i} = k_3[RMeCl]_i + v_0 \quad [11.10]$$

$$v_{4i} = k_4[MeCl_2]_i + v_0 \quad [11.11]$$

Constant k_1 is not used in calculations because reaction rate of the initial form of stabilizer is sufficiently high to prevent HCl emission, which is determined by induction period, t_0.

At induction period, stabilizer in the initial form is assumed to be sufficiently exhausted to fulfill the following condition:

$$a_{t0} = v_{2t0} \quad [11.12]$$

This means that the quantity of HCl produced, a_{t0}, at time t_0 (induction period) equals the rate of reaction of partially reacted stabilizer with HCl, v_{2t0}, at time t_0. At time t_0,

$$v_{2t0} = k_2(PA - S_{t0})a_{t0} \quad [11.13]$$

where:

v_{2t0}	rate of reaction of partially reacted stabilizer with HCl at time t_0, µmol HCl/g PVC,
k_2	reaction rate constant between RMeCl and HCl, g PVC/µmol HCl min,
PA	quantity of introduced stabilizer, µmol HCl/g PVC,
S_{t0}	quantity of HCl produced and reacted by stabilizer up to the time t_0, µmol HCl/g PVC,
a_{t0}	quantity of HCl split off in the time $(t_i - t_{i-1})$, µmol HCl/g PVC
i	time interval.

Combining equations [11.12] and [11.13]:

$$k_2 = \frac{1}{PA - S_{t0}} = \frac{1}{\Delta} \quad [11.14]$$

where:

Δ real quantity of active stabilizer at time t_0, mmol HCl/g PVC.

The following program is used to calculate constants. The input data include: name of sample, t_0, v_0, PA, limit of quantity of active stabilizer at time t_0 (μmol HCl/g PVC), Δr, k_4 (the value comes from experimental measurement as a rate of HCl emission after all stabilizer has been exhausted, it can be input as a single number or a set of pairs, kd_{4j}, Sd_{4j}, if k_4 changes with a time of degradation).

After reading input data, the program begins calculations. If $k_4 = 0$, then

$$k_2 = \frac{1}{PA - t_0 v_0} \quad [11.15]$$

and for each t_i, the following equations are fulfilled:

$$v_{2i} = k_2(PA - S_{i-1})v_0\Delta t \quad (S_0 = 0) \quad [11.16]$$

$$S_i = S_{i-1} + v_0\Delta t \quad \text{for } v_{2i} \geq v_0 \quad Wt_i = 0 \quad [11.17]$$

$$S_i = S_{i-1} + v_{2i} \quad \text{for } v_{2i} < v_0 \quad Wt_i = v_0 - v_{2i} \quad [11.18]$$

where:

S_i, S_{i-1} quantity of HCl formed and bound by stabilizer up to the times t_i or t_{i-1}, respectively, μmol HCl/g PVC,

Δt unit period of time, min.,

Wt_i quantity of HCl split off in time $t_i - t_{i-1}$, μmol HCl/g PVC

v_{2i} rate of stabilizer reaction with the second molecule of HCl, μmol HCl/g PVC min,

v_0 rate of HCl emission from composition which does not contain stabilizers, μmol HCl/g PVC min.

Next, the program calculates P_i and SW_i until stabilizer is completely consumed:

$$P_i = \frac{PA - S_i}{PA} \times 100\ [\%] \quad [11.19]$$

$$SW_i = SW_{i-1} + Wt_i \quad (SW_0 = 0) \quad [11.20]$$

For $k_4 \neq 0$, the method of calculation is more complicated. First, $\Delta = \Delta r/2$ is taken from $0 < \Delta \leq \Delta r$, and

$$k_2 = \frac{1}{\Delta} \quad [11.21]$$

Based on the values of k_2 and Δ, the constant k_3 is selected in the range $0 < k_3 \leq 4k_4$ and the following criterion is selected:

$$\left|S_t - (PA - \Delta)\right| < \varepsilon \qquad [11.22]$$

for any $\varepsilon > 0$. The quantity S_{t_0} is calculated by the following method. First, $k_3 = 2k_4$ is taken, and for each t_i $(1 \le t_i \le t_0)$, a_i and S_i are calculated:

$$a_i = (k_3 S_{i-1} + v_0)\Delta t \quad \text{for } 0 \le S_{i-1} \le PA/2 \qquad [11.23]$$

$$a_i = [S_{i-1}(k_4 - k_3) + PA(k_3 - 0.5k_4) + v_0]\Delta t \quad \text{for } PA/2 < S_{i-1} \le PA \qquad [11.24]$$

$$a_i = (0.5k_4 PA + v_0)\Delta t \quad \text{for } PA < S_{i-1} \qquad [11.25]$$

$$S_i = S_{i-1} + a_i \qquad [11.26]$$

where:

P_i	percent of active stabilizer at time t_i,
SW_i, SW_{i-1}	quantity of HCl split off up to the time t_i, μmol HCl/g PVC,
Δr	limiting quantity of active stabilizer at time t_0, μmol HCl/g PVC,
ε	any small, positive number which controls accuracy of calculations,
a_i	quantity of HCl splitting off in time $t_i - t_{i-1}$, μmol HCl/g PVC.

If the constant k_4 is given by a set of pair values of kd_{4j} and Sd_{4j}, the constant k_4 is calculated for each t_i by a linear interpolation of $Sd_{4j} \le S_{i-1} \le Sd_{4j-1}$ or $Sd_{4j} \le S_{i-1} \le PA$. If the above calculations do not fulfill condition [11.22], then the next value of k_3 is selected from the range $(0, 2k_4]$ or $[2k_4, 4k_4]$, and calculations are repeated, using equations [11.23] to [11.26]. This scheme is repeated until the condition [11.22] is met. Then, the pair of numbers k_2 and k_3 is verified. For each t_i $(1 \le t_i \le t_0)$, the following calculations are made:

$$v_{2i} = k_2(PA - S_{i-1})a_i \quad \text{for } 0 \le S_{i-1} \le PA \qquad [11.27]$$

$$v_{2i} = 0 \quad \text{for } PA < S_{i-1} \qquad [11.28]$$

If the condition

$$\left|v_{2t} - a_t\right| < \varepsilon \qquad [11.29]$$

for any $\varepsilon > 0$ is not met, then the next Δ is selected from the range of $(0, \Delta r/2]$ or $[\Delta r/2, \Delta r]$, and calculations start from point [11.21]. If the condition [11.28] is met, the constants k_2 and k_3 are accurate, and the program calculates P_i, S_i, SW_i, v_{2i}, and WT_i according to equations [11.19] to [11.20], [11.23] to [11.26], and [11.27] to [11.28] until the active stabilizer is completely exhausted:

$$S_i = S_{i-1} + v_{2i} \quad \text{for } t_i > t_0$$

$$Wt_i = 0 \quad \text{for } t_i \le t_0 \qquad [11.30]$$

$$Wt_i = a_i - v_{2i} \quad \text{for } t_i > t_0$$

Using this method of calculation, the following values of constants were obtained, as included in Table 11.2.

Table 11.2. Data on some PVC thermal stabilizers. [Data from Prochaska, K.; Wypych, G., *J. Appl. Polym. Sci*., **21**, 2113-2124, 1977.]

Stabilizer	k_2	k_3	k_4 (t_0)	% active stabilizer at t_0
Zn stearate	0.07619	0.4365	0.4460	20.77
Cd stearate	0.05079	0.0000	0.0000	33.40
Ca stearate	0.04039	0.0000	0.0000	37.57
Dibasic Pb stearate	0.01528	0.0000	0.0000	68.40
Tribasic Pb sulfate	0.00682	0.0000	0.0000	87.91

The above results show that only RZnCl catalyzes dehydrochlorination, which helps to explain the relatively short induction period of PVC stabilized with zinc stabilizers. All other results are compatible with conventional wisdom regarding mechanisms of action of these stabilizers. The above calculations and discussed methods of measurement permit generation of all data required for simulation of kinetics of degradative processes occurring in formulations containing stabilizing mixtures of metal carboxylates.

Effective simulation must account for interaction of stabilizers used in a mixture. This chemical interaction can be best explained by the following chemical equations:[85]

$$R_2Me_I + Me_{II}Cl_2 \longrightarrow Me_ICl_2 + R_2Me_{II}$$
$$R_2Me_I + RMe_{II}Cl \longrightarrow RMe_ICl + R_2Me_{II}$$
$$RMe_ICl + Me_{II}Cl_2 \longrightarrow Me_ICl_2 + RMe_{II}Cl$$
$$RMe_ICl + RMe_{II}Cl \longrightarrow Me_ICl_2 + R_2Me_{II}$$

In the following program, constant k_5 is calculated which accounts for the participation of all the above reactions. This constant is then used to correct concentrations of all active forms of stabilizers used in the mixture as well as all products of stabilizers which may have catalytic influence (RMCl and $MeCl_2$) on degradation of PVC. The value of constant k_5 is selected from the interval in which a lower limit is 0 and the upper limit is an optionally selected positive number $K5_r$. The first condition imposed on calculations causes an automatic decrease of the value of constant used for calculation if at any time, t_i, a value of reaction product of any stabilizer is smaller than 0.

At time t_0, the quantity of HCl which splits off equals the quantity of HCl bound by the stabilizers. In the case of one stabilizer, this condition can be expressed as follows:

$$v_{2t_0} = k_2[RMeCl]a_{t_0} \qquad [11.31]$$

Since

$$v_{2t_0} = a_{t_0} \qquad [11.32]$$

it follows that

$$k_2[RMeCl] = 1 \qquad [11.33]$$

This means that it is assumed that a stabilizer in its original form has sufficiently high reactivity to completely react before time t_0. Because we calculate kinetics for a mixture of stabilizers, the constant k_5 has such a value that condition [11.33] is fulfilled for at least one stabilizer. The program begins with reading and printing of input data, as follows:

v_0	rate of degradation of PVC without stabilizers,
t_0	time of beginning of HCl emission (induction period),
$K5_r$	limiting value of constant of rate of reaction of chlorine exchange,
PA_l	stabilizer reaction capability (see Table 11.1)
$K1_l$	constant of reaction rate between R_2Me and HCl,
$K2_l$	constant of reaction rate between RMeCl and HCl,
$K3_l$	constant of degradation rate in presence of RMeCl,
K4l	constant of degradation rate in presence of $MeCl_2$,
$Kd3_{j,l}$, $Sd3_{j,l}$	constant k_3 and k_4 for stabilizers whose products of reaction affect nonlinearly the
$Kd4_{j,l}$, $Sd4_{j,l}$	degradation kinetics, expressed in proportion to concentrations of the products,
Δt	unit period of degradation time,
l	index (l = 1,2) represents the stabilizer number,
i	index (i = 1,2,...,t_0,...,100) marks time intervals, t_i.

When index l exists in any equation, the value is calculated for both stabilizers, while index 1 or 2 marks values or equations concerning the first and the second stabilizer.

It is accepted in the program that the stabilizer with index 1 is the chlorine acceptor from reaction products with HCl of the stabilizer marked 2.

After reading the data, the program looks for the value of constant K5 in the range $(0, K5_r]$ by using a sectional method. First, K5 = 0 and next for $K5 = K5_r/2$, output data are calculated for each $t_i \in [1, t_0]$ using the following equations:

$$a_i = \Delta t\left[\sum_{l=1}^{2}(K3_l S1_{i-1,l} + K4_l S2_{i-1,l}) - v_0\right] \text{ and } S1_{0,l} = S2_{0,l} = 0 \qquad [11.34]$$

$$UK1_{i,l} = \frac{a_i K1_l P_{i-1,l}}{\sum_{l=1}^{2}(K1_l P_{i-1,l} + K2_l S1_{i-1,l})} \text{ and } P_{0,l} = \frac{PA_l}{2} \qquad [11.35]$$

$$UK2_{i,l} = \frac{a_i K2_l P_{i-1,l}}{\sum_{l=1}^{2}(K1_l P_{i-1,l} + K2_l S1_{i-1,l})} \qquad [11.36]$$

$$VK1_{i,l} = K1_l P_{i-1,l} UK1_{i,l} \qquad [11.37]$$

$$VK2_{i,l} = K2_l P_{i-1,l} UK2_{i,l} \qquad [11.38]$$

$$V5_i = K5(P_{i-1,l} + S1_{i-1,l})(S1_{i-1,2} + S2_{i-1,2}) \qquad [11.39]$$

$$U51_i = V5_i \frac{P_{i-1,l} K1_l}{P_{i-1,l} K1_l + S1_{i-1,l} K2_l} \quad [11.40]$$

$$U52_i = V5_i \frac{S1_{i-1,l} K2_l}{P_{i-1,l} K1_l + S1_{i-1,l} K2_l} \quad [11.41]$$

$$U53_i = V5_i \frac{S1_{i-1,2}}{S1_{i-1,2} + S2_{i-1,2}} \quad [11.42]$$

$$U54_i = V5_i \frac{S2_{i-1,2}}{S1_{i-1,2} + S2_{i-1,2}} \quad [11.43]$$

$$S1_{i,1} = S1_{i-1,1} + UK1_{i,1} + U51_i - UK2_{i,1} - U52_i \quad [11.44]$$

$$S1_{i,2} = S1_{i-1,2} + UK1_{i,2} + U53_i - UK2_{i,2} + U54_i \quad [11.45]$$

$$S2_{i,1} = S2_{i-1,1} + UK2_{i,1} + U52_i \quad [11.46]$$

$$S2_{i,2} = S2_{i-1,2} + UK2_{i,2} - U54_i \quad [11.47]$$

There are several limitations imposed on the above equations, as follows. If in equations [11.44] or [11.45], $S1_{i,l} < 0$ then $S1_{i,l} = 0$ is taken. If in equation [11.46] or [11.47] $S2_{i,l} > PA_l/2$, then $S2_{i,l} = PA_l/2$. If in equations [11.44] or [11.45] $VK1_{i,l} < UK1_{i,l}$ or $VK2_{i,l} < UK2_{i,l}$ then $UK1_{i,l} = VK1_{i,l}$ or $UK2_{i,l} = VK2_{i,l}$ is taken.

If for any $t_i \in [1, t_0]$ $S2_{i,l} < 0$, the value of constant k_5 is decreased and the program returns to calculation of a_i at $t_i = 1$. After performing calculations for time t_0, the accuracy of constant k_5 is inspected. The constant k_5 is precise when for $l = 1$ or 2:

$$\left| K2_l S1_{t_0,l} - 1 \right| < \varepsilon \quad [11.48]$$

for any $\varepsilon > 0$ selected. If condition [11.48] is not fulfilled as in the case when $K2_l S1_{t_0,l} > 1$, k_5 is decreased, and in reverse case, k_5 is increased. Calculations then begin from a_i.

When accuracy of k_5 is satisfactory, the program calculates all output data (see a list below) in the interval $t_0 < t_i \leq 100$ and Wt_i and SWt_i (up to t_0, $WT_i = 0$):

$$Wt_i = \sum_{l=2}^{2} UK1_{i,l} - VK1_{i,l} + \sum_{l=1}^{2} UK2_{i,l} - VK2_{i,l} \quad [11.49]$$

$$SWt_i = SWt_{i-1} + Wt_i \quad [11.50]$$

If any difference in equation [11.49] is negative, then it is replaced by zero.

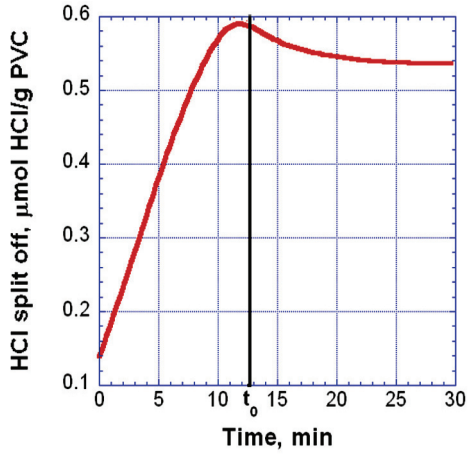


Figure 11.6. HCl formation during degradation of PVC formulation containing a mixture of calcium and zinc stearates. [Adapted, by permission, from Prochaska, K.; Wypych, G., *J. Appl. Polym. Sci*., **23**, 2031-2042, 1979.]

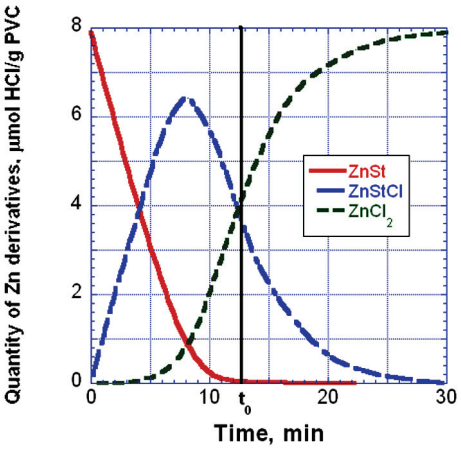


Figure 11.7. Changes in quantities of Zn stearate, Zn stearate reacted with one molecule of HCl, and $ZnCl_2$ during thermal degradation of PVC formulation stabilized by a mixture of calcium and zinc stearates. [Adapted, by permission, from Prochaska, K.; Wypych, G., *J. Appl. Polym. Sci*., **23**, 2031-2042, 1979.]

Output data:

a_i	quantity of HCl split off in time $t_i - t_{i-1}$,
$UK1_{i,l}$	quantity of HCl reacting with stabilizer l,
$UK2_{i,l}$	quantity of HCl reacting with partially reacted stabilizer l,
$U51_i$	quantity of stabilizer in initial form – chlorine acceptor (e.g., Ca stearate),
$U52_i$	quantity of partially reacted stabilizer – chlorine acceptor (e.g., CaStCl),
$U53_i$	quantity of stabilizer in initial form – chlorine donor (e.g., Zn stearate),
$U54_i$	quantity of partially reacted stabilizer – chlorine donor (e.g., ZnStCl),
$VK1_{i,l}$	potential rate of HCl bonding by stabilizer l in the initial form (e.g., $MeSt_2$),
$VK2_{i,l}$	potential rate of HCl bonding by stabilizer l in the partially reacted form (e.g., MeStCl),
$V5_i$	total rate of interacting stabilizers,
$S1_{i,l}$	quantity of RMeCl formed,
$S2_{i,l}$	quantity of metal chloride formed,
$P_{i,l}$	quantity of stabilizer l in the initial form,
$PR_{i,l}$	percent of unreacted stabilizer l,
Wt_i	quantity of HCl emitted in period of time: $t_i - t_{i-1}$,
SWt_i	quantity of HCl emitted up to the time t_i.

Figures 11.6 and 11.7 show the results of calculation of the degradation process of PVC stabilized by a mixture of Zn/Ca stearates.[85] HCl formation increases rapidly in the beginning of the degradation process to reach a maximum just before HCl begins to be emitted outside the sample. The rate of HCl formation then slightly decreases to reach a plateau. Figure 11.7 shows that at the time when emission of HCl begins, the initial form of Zn stearate has been almost completely exhausted and about the half of zinc chloride is present, which causes a dramatic increase in dehydrochlorination rate.

The proposed method of studies of mixed metal carboxylates is relatively simple from an analytical point of view since it does not require complex equipment and time-consuming research. Also, calculation of results is straight-forward, producing a large amount of data useful in analysis of degradation and stabilization processes.

11.3 STABILIZER GROUPS

All stabilizer groups are discussed according to the following breakdown:

- commercial stabilizers
- properties
- applications
- mechanisms of action
- costabilizers
- research findings.

Information on commercial stabilizers, their properties, and applications are presented in the form of a table. The information on commercial stabilizers is not complete because some major manufacturers of stabilizers chose to keep even the most generic information secret. It is therefore not possible to assign names of stabilizers to their groups. In many cases, even simple data on commercial stabilizers are not available.

The discussion of the mechanisms of stabilizers takes advantage of stabilizer function already discussed in Section 11.1 of this chapter in order to avoid unnecessary repetitions. Information on costabilizers is based on research data and patent literature and it outlines options used presently and in the past.

The research findings section considers all publications relevant to a particular group of stabilizers to show findings and gaps.

11.3.1 METAL SOAPS

11.3.1.1 Barium/zinc

11.3.1.1.1 Properties and applications of commercial stabilizers

Table 11.3. Properties and applications of barium/zinc stabilizers

Manufacturers: Galata Chemicals; Ferro; AM Stabilizers Corporation; Akcros; Baerlocher			
Commercial names: Mark 398, 2181, 4117, 4159, 4520, 4712, 4716, 4727, 4734, 4754LV, 4781A, 4821, 4822A, 4825, 4830, 4847P, 4848, 4852, 4864, 4880, 6042 ACM, 6062, 6708, 6708 ACM, 6710 ACM, 6734, 6777 ACM, 9304, 9314, RFD; Therm-Chek 142, 6581, SP 175, SP 1960, SP 210, SP 1363; Plastistab 2372; Lankromark LBZ248, LBZ320, LBZ413, LBZ693, LBZ792, LBZ968; Baerostab KK40, KK40-1, UBZ 171 T, UBZ 637, UBZ 644 X, UBZ 660, 667, UBZ 720-1, UBZ 711 X, UBZ 720-1, UBZ 776 X			
Chemical name: barium-zinc carboxylate			
Mol. weight: 407-704	**Melting**, ^{o}C: n/a	**Decomp.**, ^{o}C: 454-522	**Flash point,** ^{o}C: 40-120
Ref. index: 1.47-1.52	**Density**, 20^{o}C: 0.93-1.17	**Viscosity**, mPas: 50-4500	**Vapor pres**., Pa: n/a
State: solid and liquid	**Color**: white to amber	**Color (Gardner)**: 4-8	**Odor**: n/a
Composition: Ba:Zn=3:1 to 3:5 (kicker); acids C10 to C18			
Exceptional properties: good color and transparency, high efficiency, some grades are formulated as low phenol (nonyl phenol free), low VOC (low-fogging), fast kickers, light and aging stability, lubricating properties, excellent aged plastisol viscosity, replacement for cadmium and lead stabilizers, eliminates staining associated with cadmium-containing stabilizers, good plate-out characteristics, good resistance to copper greening, good printability, some grades are formulated with low phosphite content which eliminates exudation under hot humid conditions			
PVC processing methods: calendering, coating, dip coating, coil coating, extrusion, injection molding, slush molding, rotational molding			
Product applications: flexible PVC, plastisols, flexible films and sheets, semi-rigid compounds, topcoat and basecoat in flooring; artificial leather (also automotive use); arm rests and interior parts of automobile; automotive body side parts; kickers in artificial leather and wallcoverings; base and top coats of outdoor products such as roofing, tarpaulins, tents, banners, and sun-protections; car underbody sealants; conveyor belts; Evaloy containing materials; wire & cable jacketing, swimming pool liners, flexible profiles and tubes, coil coated steel, toys, medical tubing, refrigerator gaskets			
Recommended addition rates, phr: 1.5-3.5			

11.3.1.1.2 Mechanisms of action

Both barium and zinc components of the mixture participate in reactions with HCl as discussed in Section 11.1.1. This action diminishes catalytic influence of HCl on degradation rate and prolongs stability. Zinc component of the mixture is active in removal of labile chlorine atoms as discussed in Section 11.1.2. Other essential parts of the mechanism are discussed in Section 11.2.3, which contains information on the catalytic effect of zinc carboxylate partially reacted with HCl and zinc chloride. Section 11.2.3 also includes information on exchange of chlorine between barium carboxylate and chlorine-containing reaction-products of zinc component with HCl, which are relevant to the mechanisms of these stabilizers.

Bacaloglu *et al*.[87] determined characteristic constants of PVC degradation and stabilization of wire and cable compounds stabilized with Ba/Zn and Ca/Zn stabilizers (for further discussion of Ca/Zn stabilizer and comparison of both types of stabilizers see the next section). In the case of Ba/Zn stabilizer, both constants (Figures 11.8 and 11.9) have the almost linear relationship with temperature. The values of constants increase with temperature quite rapidly.[87]

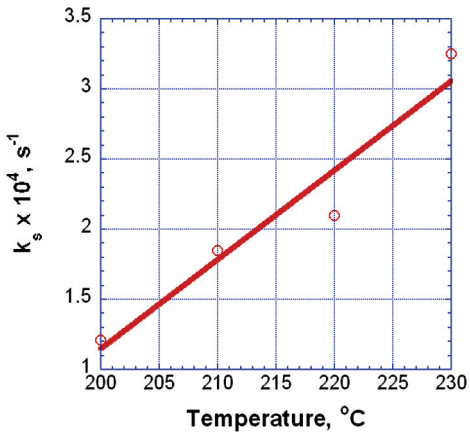


Figure 11.8. Constant of early color, k_s, for wire and cable compound stabilized with Ba/Zn stabilizer. [Data from Bacaloglu, R.; Fisch, M.; Steven, U.; Bacaloglu, I.; Krainer, E., *J. Vinyl Additive Technol.*, **8**, 3, 180-193, 2002.]

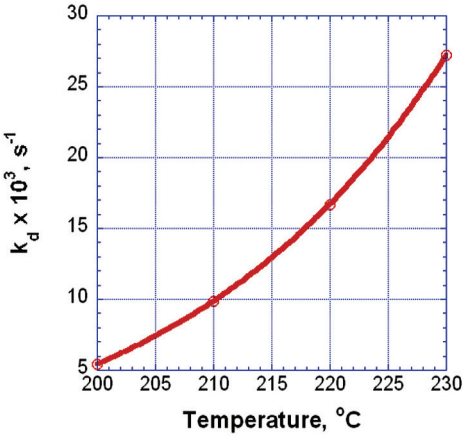


Figure 11.9. Constant of degradation, k_d, for wire and cable compound stabilized with Ba/Zn stabilizer. [Data from Bacaloglu, R.; Fisch, M.; Steven, U.; Bacaloglu, I.; Krainer, E., *J. Vinyl Additive Technol.*, **8**, 3, 180-193, 2002.]

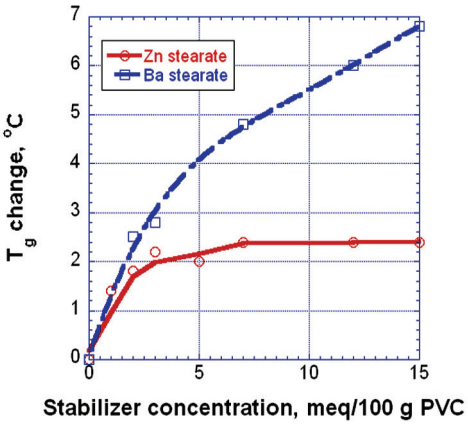


Figure 11.10. Changes in the glass transition temperature of PVC vs. concentration of stabilizer. [Data from Fisch, M. H.; Bacaloglu, R., *J. Vinyl Additive Technol.*, **4**, 1, 39183, 1998.]

Fisch and Bacaloglu[88] determined the glass transition temperature of PVC containing variable amounts of Ba and Zn stearates (Figure 11.10). They found that Zn stearate affects glass transition temperature to a lesser extent than Ba stearate. In the range of concentrations studied, Zn stearate influence levelled off, whereas the Ba stearate effect was still growing.[88] If the temperature difference is small, as is the case of Zn stearate, then it is considered that stabilizer is an external lubricant. If the temperature difference is larger, as in the case of Ba stearate, then it indicates that stabilizer is able to affect chain flexibility and such stabilizer is considered to be an external/internal lubricant. The study underlines the roles of both components and it also shows that with a selection of proper acid Ba/Zn stabilizer has self-lubricating properties. The lubricating properties of a particular stabilizer have to be accounted for in selecting the formulation.

11.3.1.1.3 Costabilizers

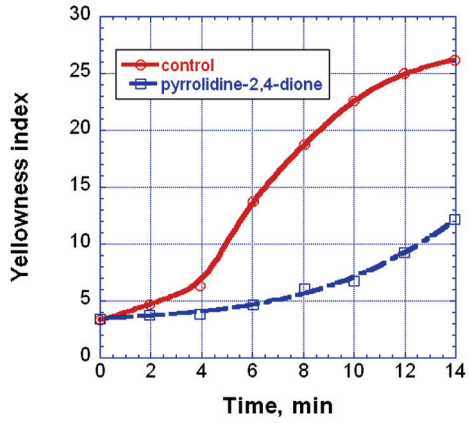
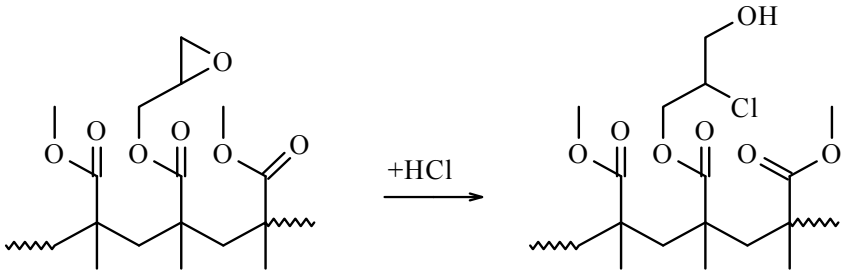


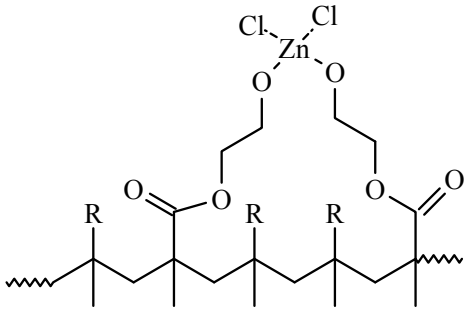
Figure 11.11. Yellowness index of formulation at 180°C with and without 1.3% pyrrolidine-2,4-dione vs. time of heating. [Data from Burley, J. W., *J. Vinyl Additive Technol.*, **3**, 3, 205-209, 1997.]

Section 11.1.3 provides information on the mechanism of costabilization of phosphites. In the earlier stages of stabilization development, phosphites were the major costabilizers used with Ba/Zn carboxylates to reduce catalytic influence of $ZnCl_2$ on degradation rate and to prolong stability of PVC formulation. Section 11.1.4 discusses the mechanism of costabilization by dienophiles. Their use is now very common in PVC stabilization with Ba/Zn carboxylates. Figure 11.11 shows the dramatic changes in PVC color stabilization in the presence of pyrrolidine-2,4-diones.[89] In addition to elimination of labile chlorines as shown in Section 11.1.4, polyketones are also able to complex zinc chloride.[90,91] In addition to complexing $ZnCl_2$, which reduces its catalytic activity, polyketones also form complexes with zinc carboxylates. Depending on the type of the polyketone, dissociation of active stabilizer is either easier or more difficult. Akcros patented use of pyrrolidine-2,4-dione because it has a good balance of binding chloride and releasing active stabilizer.[92] Improvement in stabilization is also achieved because of self-lubricating properties of Ba/Zn stabilizer used in combination.[91]

Methacrylate-based copolymers with 2-hydroxyethyl methacrylate and 2,3-epoxypropyl methacrylate were found to improve the induction period of PVC dehydrochlorination. The costabilizing effect depends on the amount of functional groups in copolymer. The costabilizers interact with most used types of stabilizers. Costabilizers drastically increased induction times (5.9 times) of Ba/Zn carboxylates.[93] It is believed that costabilizers act by HCl binding



and interaction with $ZnCl_2$



$R = CO_2CH_3$

both of which reduce catalyzed dehydrochlorination. $ZnCl_2$ binding can be either an intramolecular (as shown) or intermolecular process.[93]

11.3.1.1.4 Research findings

Mold staining and amine resistance were once an important difficulty to overcome in powder molding. Mold staining occurs because of deposition of tacky substances on the surface of the mold which are difficult to remove. In addition to staining the surface of molded material, it becomes glossy, which is frequently undesirable.[94,95] It was discovered that application of a mixture of barium and zinc salt of carboxylic acids can be successfully used to remediate the problem if metal salts have melting temperatures above 250°C.[94,95] Hydrotalcite containing perchlorate ion was also a part of the package used for stabilization. The addition of hydrotalcite was found to give excellent amine resistance to the composition.[94,95] There is a long list of suitable metal salts which have a melting point above 250°C. In the reported studies oxalates, malonates, maleates, tartrates, benzoates, and p-tert-butylbenzoates were successfully used.[94,95]

Swimming pool chemicals and pool liner cleaners affect UV degradation of PVC liners, especially along the waterline.[96] This causes a development of dark discoloration around the top of the liner immediately above the waterline. Barium/zinc-alkyl phosphite stabilizer in conjunction with benzophenone type UV absorber has been found to be suitable stabilizer to prevent such effects.[96]

PVC stabilized with a mixture of Ba/Zn laurates used together with hydrotalcite, dibenzoyl methane, and calcium terephthalate was used in the formulation of lead-free wire and cable. Both good stability and insulating effect were achieved.[97]

Printability problems with barium/zinc stabilizers have been associated with the migration of a 1:1 Ba/Zn stearate complex to the PVC surface.[98] Surface hydrolysis resulted in formation of a basic mixed Ba/Zn stearate complex and liberation of free stearic acid. The liberated stearic acid may cause inferior printability because Ba/Zn stabilizers are widely used and only isolated incidences of printability problems have been reported. It seems that many factors may influence the printability of flexible vinyl films and proportion of stearates is one of them.[98] In the patented application,[99] Ba/Zn carboxylates were used in combination with triphosphites ($R_1OP(OR_3)OR_2$) and phosphites

($R_4OP(OH)OR_5$) to improve heat-mediated deterioration. This composition improved wettability of film and adherence to water based inks.[99] This seems to indicate that Ba/Zn stabilizers are useful in printable films but composition must be properly selected to prevent surface changes during processing.

The use of zinc-containing biocides in PVC has been limited to plastisol formulations, which are not subjected to the heat and shear histories of calendered and extruded formulations.[100] Patented technology[101] has been developed to overcome problems related to the addition of zinc-containing biocides to PVC. The use of hydrotalcites in combination with zinc pyrithione improved sensitivity to heat and shear as well as retention of the antimicrobial activity of the zinc additive.[100] Hydrotalcite acts in this formulation as acid scavenger.[100] Ba/Zn stabilizers are compatible with a range of popular fungicides such as 10,10-oxybisphenoxarsine, 2-n-octyl-isothiazolin-3-one, and 4,5-dichloro-2-n-octylisothiazolin-3-one.[102]

A recent invention seems to offer an alternative to Ba/Zn stabilizers.[103] A small addition of sodium perchlorate in combination with polyethylene glycol gives better stabilizing performance than Ba/Zn stabilizer in calendering formulations.[103] In plastisol compositions these two are accompanied by epoxy resin.

Ba/Zn stabilizers are very toxic to aquatic organisms.[104]

11.3.1.2 Calcium/zinc

11.3.1.2.1 Properties and applications of commercial stabilizers

Table 11.4. Properties and applications of calcium/zinc stabilizers

Manufacturers: Galata Chemicals, Ferro, Dover, AM Stabilizers Corporation, Akcros, Baerlocher			
Commercial names: Mark 152, 152S, 593, 1034, 1034K, 1146C, 1221, 1495C, 2129, 3023, 3118, 3123A, 3710, 4119, 6092 ACM, 6765 ACM, 6782, 6783 ACM, 6784 ACM, QTS; Therm-Chek 659, 760X, 5760, SP 239, SP 1795; Doverlub CA-20, CA-21, CA-22, (all (1)), ZN-20, ZN-20 (both (2); Plastistab PS2120 to PS2199; Interlite ZP7003, ZP8691, ZP9600, ZP9604, ZP9623, ZX9011, ZX9050, Lankromark LZC107, LZC393, LZC448, LZC749, LZC803; Baerostab L 233 (5), L 140-100 (5), L 141-100 (5), CT 9162, NT 1 S, NT 170 PS, NT 170 PS, NT 319 P, NT 326 D, NT 560 A, NT 1800 N, NT 324-1 P (2), CT 9161 X, CT 9162 X, CT 9169 X, CT 9173 X			
Chemical names: calcium/zinc carboxylate, calcium carboxylate (1), zinc carboxylate (2), overbased carbonated Ca (3), overbased carbonated Zn (4); zinc octoate (5)			
Ref. index: 1.45-1.50	**Melting**, ºC: 155 and up	**Density**, 20ºC: 0.92-1.15	**Flash point,** ºC: 60->260
State: liquid, paste, solid	**Color**: white to yellow	**Color (Gardner)**: 4-10	**Odor**: odorless to mild
ACGIH, mg/m^3: 10	**OSHA**, mg/m^3: 5-15	**LD50, rat**, g/kg: >10	**log Kow**: n/a
Composition (available grades): phosphite-free; low phenol, nonylphenol-free, ethylenehexanoic acid-free, butylbenzoic acid-free, bisphenol A-free. Zn:Ca=1:4 to 2:1; acids: C_8 to C_{18}			
Exceptional properties: non-toxic, excellent color and clarity, no influence on taste or odor, low fogging, low odor, good weatherability, no tendency to plate out, eliminates sulfide stain, replacement to cadmium and lead-based stabilizers			
PVC processing methods: calendering, coating, coil coating, dip coating, extrusion, rotational molding			
Product applications: kicker (5), basecoat of CV flooring, carpet backing, sealing compound for closures, topcoat & basecoat in flooring, leather for automotive use, wall coverings, outdoor applications (roofing, tarpaulins, tents, banners, sun protections), underbody sealants, conveyor belts, film, refrigerator gaskets, tubes, toys, articles for food contact applications, window profiles, power cable, automotive parts, medical, pipe, siding, wire and cable, gloves, translucent sheet, roofing membranes, pond liners, coated fabrics, door strip			
Recommended addition rates, phr: 0.75 to 4			

11.3.1.2.2 Mechanisms of action

Both calcium and zinc components of the mixture participate in reactions with HCl as discussed in Section 11.1.1. This action diminishes catalytic influence of HCl on degradation rate and prolongs stability. Zinc component of the mixture is active in removal of some labile chlorine atoms as discussed in Section 11.1.2. Other essential parts of the mechanism are discussed in Sections 11.2.2 and 11.2.3, which contain information on the catalytic effect of zinc carboxylate partially reacted with HCl and zinc chloride. Sections 11.2.2 and 11.2.3 also include information on exchange of chlorine between calcium carboxylate and chlorine-containing reaction-products of zinc component with HCl, which are relevant to the mechanisms of these stabilizers.

Bacaloglu *et al*.[87] determined characteristic constants of PVC degradation and stabilization of wire and cable compounds stabilized with Ba/Zn and Ca/Zn stabilizers (discussion of Ba/Zn stabilizer is included in Section *11.3.1.1.2* and Figures 11.8 and 11.9 contain the relevant data). Figures 11.12 and 11.13 show relationships between temperature and constants k_s and k_d for Ca/Zn stabilizers. The values of constants also increase with temperature quite rapidly as for Ba/Zn stabilizer.[87] The early color, evaluated by the degradation in the stabilization period (constant k_s) is better in the case of Ca/Zn. The degradation rate constants k_d (after the stabilization period is ended) are very different.[87] In the case of the Ba/Zn stabilizer, a fast discoloration shows that after the Ba/Zn carboxylate complex is used, there is no more barium carboxylate excess available and a fast degradation catalyzed by $ZnCl_2$ occurs.[87] In the case of the Ca/Zn stabilizer, there is still some calcium car-

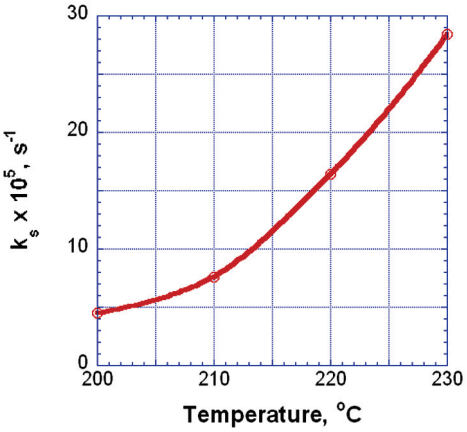


Figure 11.12. Constant of early color, k_s, for wire and cable compound stabilized with Ca/Zn stabilizer. [Data from Bacaloglu, R.; Fisch, M.; Steven, U.; Bacaloglu, I.; Krainer, E., *J. Vinyl Additive Technol.*, **8**, 3, 180-193, 2002.]

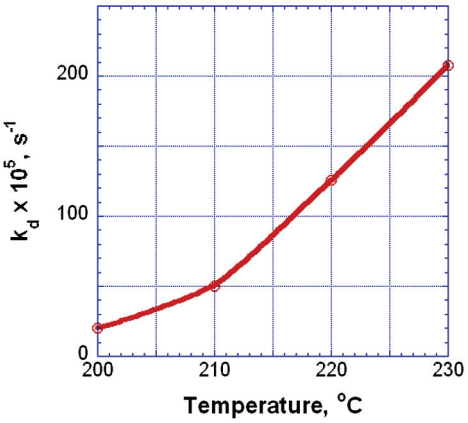


Figure 11.13. Constant of degradation, k_d, for wire and cable compound stabilized with Ca/Zn stabilizer. [Data from Bacaloglu, R.; Fisch, M.; Steven, U.; Bacaloglu, I.; Krainer, E., *J. Vinyl Additive Technol.*, **8**, 3, 180-193, 2002.]

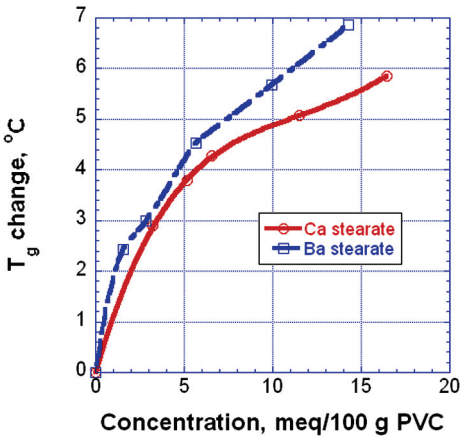


Figure 11.14. Changes in the glass transition temperature of PVC vs. concentration of stabilizer. [Data from Fisch, M. H.; Bacaloglu, R., *J. Vinyl Additive Technol.*, **4**, 1, 39183, 1998.]

boxylate present that plays the role of HCl scavenger while the zinc remains blocked in a complex with a costabilizer (note that performance of stabilizer is improved by costabilizer; see more on this topic below).

Ba/Zn stabilizer and Ca/Zn have a similar lubricating properties (Figure 11.14 shows that Ba and Ca stearates have similar glass transition temperatures and the discussion of data in Figure 11.10 also applies here).[88]

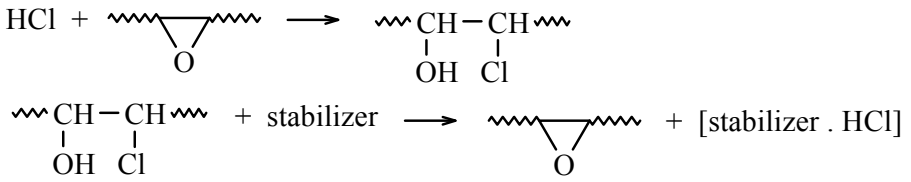
11.3.1.2.3 Costabilizers

Ca/Zn stabilizers were in the past considered to be too expensive and not sufficiently efficient, therefore they were not a leading group of stabilizers in spite of the fact that they are non-toxic. The current view on these stabilizers has changed because several groups of other stabilizers are either not used or are in limited use now. The question of price was addressed by a larger production which made these stabilizers more cost-effective. They performance was mostly enhanced by proper use of costabilizers.

In the past, calcium/zinc stabilizers were frequently prepared in the form of a dispersion in epoxidized oil, which is usually added to stabilizing compositions anyway. Epoxi-

dized oil can be easily detected in the IR spectrum through the ester absorption band at 1720 cm^{-1}. However, the presence of this peak does not necessarily mean that epoxy compound was added because ester groups may come from a lubricant or other component of formulation.

The mechanism of action of epoxy stabilizers was proposed by this author, as follows:[105]



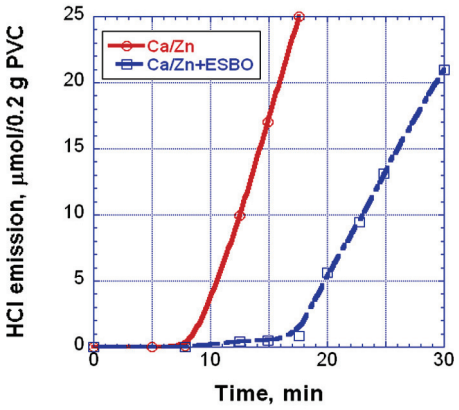


Figure 11.15. Emission of HCl from PVC sheets containing Ca/Zn=1:1 stearates with and without epoxidized soybean oil vs. time of heating at 180°C. [Data from Benaniba, M. T.; Belhaneche-Bensemra, N.; Gelbard, G., *Polym. Deg. Stab.*, **74**, 3, 501-505, 2001.]

Epoxy costabilizer reacts with HCl and transfers it to the main stabilizer. Because of these reactions, free HCl is reacted faster (less catalytic influence) and the system is able to accommodate some quantities of evolved HCl even after primary stabilizer is exhausted. This mechanism of action was concluded on the basis of experimental data.[105]

Figure 11.15 shows results of testing PVC formulation with and without costabilizer. Costabilizer substantially delays emission of HCl.[106,107] Ca/Zn stabilized systems with epoxy costabilizers were patented, offering improvements in system stability.[108,109]

Similar to Ba/Zn stabilizers (see Figure 11.11), pyrrolidine-2,4-dione, P24D, improves quality of Ca/Zn stabilizers.[89] In addition to a better color retention, P24D reduces haze and plateout and improves weather resistance of formulation as tested by QUV.[89] A patented system[110] has been developed to stabilize unplasticized molding composition of PVC without use of toxic metals such as cadmium or zinc. The stabilizing mixture contained Ca/Zn carboxylates (stearate, octoate, behenate)=2:1 to 1:1, β-diketone, and alkaline metal oxide (e.g., magnesium oxide). This formulation was utilized in molding and extrusion of window profiles and pipes.

Basic calcium/aluminum hydrophosphites ($Ca_2Al_2(OH)_{2(z+2)}HPO_3.pH_2O$) have been successfully used as a costabilizers of zinc stearate in calendering of semi-rigid and flexible film.[111] Addition of hydrotalcite in this formulation further increased thermal stability of PVC stabilized with Zn stearate.[111] The use of hydrotalcite in conjunction with Ca/Zn stabilizer was beneficial in production of wire and cable without lead stabilizers.[112] Formulation containing hydrotalcite and Ca/Zn stabilizers was also weather resistant.[112] In

another invention, hydrotalcite was replaced by garnet containing various compositions of metals incorporated into aluminosilicate lattice (e.g, $Ca_aAl_bSi_2O_8(SiO_4)_c(OH)_d$). Incorporated metals included Na, Ti, and Zr.[113] The invented composition increases initial discoloration time threefold. This formulation was still another method of replacing lead and cadmium containing stabilizers.

The overbased carboxylate salts (including Ca/Zn carboxylates) have been developed to obtain a liquid form of stabilizer but without volatiles which cause fogging.[114-116] Overbased mixture was obtained by reacting zinc oxide with stearic acid, adding aromatic acid and reacting either calcium or magnesium oxide under controlled heating conditions to minimize side reactions.[114] The product of this reaction causes no fogging and gives good thermal stability. A shelf-stable liquid overbased calcium carboxylate can be obtained by reaction of calcium base with a monocarboxylic acid, and carbonating in the presence of phenol and alcohol.[115] Product of this reaction can be mixed with zinc carboxylate to obtain a stabilizing mixture providing heat stability, clarity and improved plateout properties.[115] Phosphites are excellent costabilizers of this system.[115] Ternary system of liquid overbased Ca/Ba/Zn carboxylates has the same excellent properties, including thermal stability, early color, clarity, and plateout.[116] Low-volatile Ca/Zn stabilizer may contain also monohydric alcohol with 12 or more carbon atoms as diluent.[117] Emission of volatiles from PVC stabilized with this composition is 1000 $\mu g/m^2$/hour or less, which makes it a good stabilizer for products used indoors.[117]

Triketone, dibenzoyl methane, and dehydroacetic acid were used as costabilizers for Ca/Zn metal carboxylates.[118] The triketone exhibited a remarkable ability to form coordination compounds with the metal soaps, even on simple mixing.

11.3.1.2.4 Research findings

Stabilizers in this group have a full variety of applications in the processing of rigid, semirigid, and plastisols. Their main advantage is their low toxicity, which allows them to be used in products in contact with food and pharmaceuticals, and also in PVC materials applicable in medicine. These stabilizers are divided into two classes, low-toxic and nontoxic, the main difference between them being the type of acid used. Low-toxic stabilizers contain lower fatty acids, including C15 (identified by their retention time, which is between that of myristic and palmitic acids). Non-toxic stabilizers are produced on the basis of stearic acid, which is likely obtained from natural raw materials, since it usually contains admixtures of other naturally occurring acids such as palmitic, lauric, and myristic.

There seems to be no rule regarding what the proportion of metals should be. It is obvious from the properties of these two metals that if the amount of zinc is increased, it should result in better initial color preservation and better clarity, while in the opposite case, better long-term stability is achieved. Therefore, depending on the possible application of the stabilizer, proper composition can be chosen as a full variety of products is available. At the same time, the application of costabilizers may drastically change these performance characteristics, permitting use of high zinc stabilizers, as can be seen from the information in the previous section. The lubricating properties of these stabilizers are fairly good, especially those of the longer fatty acids, but in the processing of rigid PVC it

is still necessary to adjust lubrication, which can be as simple as a small addition of stearic acid.

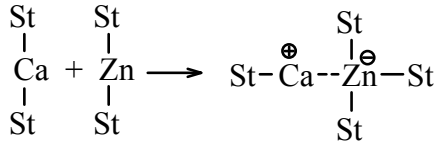
It is evident from the previous section that the zinc carboxylate without calcium component can give good performance providing it is supported by costabilizer(s), especially products which interfere with catalytic activity of zinc chloride. Calcium carboxylate alone has only limited relevance to PVC stabilization because its compositions darken well before HCl begins to be detected in the surrounding atmosphere.[119] Therefore its reactivity with HCl alone is not sufficient to make it perform as a PVC thermal stabilizer. At the same time, its presence in a formulation is usually important for thermal stability. Braun[120] has demonstrated this very well on the basis of supplemental stabilization of recyclate. If 10 phr of chalk was added to recycled PVC, its thermal stability measured by HCl emission was enhanced. This will be of even more value if Ca/Zn was the original stabilizer.

It also should be noted that original materials are usually stabilized in excess to compensate for eventual errors. It is also well reported that stabilizers are only marginally used during a material cycle. It is not infrequent to find that over 90% stabilizing activity is still present after 20 years of material use. In one experiment, indoor profiles of PVC were re-extruded from one to five times without adding new additives.[121] The material was characterized after each extrusion using measurements of color, degree of gelation, stress–strain at break and UV-vis-NIR spectroscopy.[121] The material showed an improvement of mechanical properties after the second extrusion. The estimated lifetime for indoor use at room temperature for the material after five extrusions was one-third of the lifetime of the material extruded only once.[121] A long lifetime can be expected even for material subjected to five consecutive extrusions.[121]

Conjugated double bonds absorb light and their absorption is shifted to longer wavelengths as the number of double bonds increases. If the number of double bonds is eight or more, the absorption is in the blue region of the visible spectrum and material yellows. The most distinct difference between various numbers of extrusions in the previous experiment was observed within the wavelength range 420–480 nm, which corresponded to polyene sequences having 10–14 conjugated double bonds.[121]

No significant quantities of polyene are produced before Ca/Zn stabilizer is exhausted.[122] At the same time, carbonyl and hydroxyl group concentration increases on exposure to UV radiation in QUV.[123] This illustrates very well stabilization with Ca/Zn carboxylates. It is very easy to protect PVC against thermal degradation using Ca/Zn stabilizers. In the case of recycling, stabilizers are usually active, and if need be they can be very easily supplemented even using calcium-containing fillers. But this only regards materials which are to be used indoors. If materials are exposed to UV radiation, Ca/Zn stabilizers have very little to do with PVC protection because they do not have the ability to decrease formation of hydroxyl and carbonyl groups and therefore other means have to be used to provide this protection (see below discussion of UV stabilizers in the separate sections). It is claimed in a recent invention that addition of calcium carbonate protects articles made out of rigid PVC from external exposure to heat and sunlight.[123]

Several studies[124-127] show Ca/Zn stearates form a complex on preheating to melt stabilizers together. The following formula characterizes the process:



It is reported that preheating enhances the stabilizing abilities of the complex.[124-125] The presence of this complex was confirmed by FTIR and X-ray diffraction studies. It is suggested[125] that preheating of $ZnSt_2$ makes it more free to coordinate with allyl chlorine and to exchange carboxylates with $CaSt_2$. It was concluded, based on the study of the effect of preheating on stabilizing effectiveness of various mixtures of stabilizers, that, in formulations containing epoxidized soybean oil and both stearates, preheating reduces the HCl release; but thermal stability measured by color remains generally unchanged.[127,131]

In summary, Ca/Zn stabilizers benefited from the urgent need to replace lead and cadmium stabilizers[128,129] which had a long history of good performance in wire and cable, pipe and window profiles (to include the most important products). These changes were also made possible because of new developments in costabilizers, as discussed in the previous section. It is believed that future efforts will continue to focus on Ca/Zn stabilizers as heavy metal-free alternatives to some other metal carboxylates (e.g., Ba/Zn).[130] Elimination of phenol-based products, which is already on the way, will produce truly "green" stabilizers. In conjunction with effective application and testing, these stabilizers may prove to be effective in many products used today.

Basic zinc cyanurate was more efficient PVC stabilizer than zinc stearate.[132] It delayed fast degradation of PVC at the end of a full use of the stabilizer, which is typical of zinc stabilizers.[132] This is attributed to the strong ability of the cyanurate anions to absorb the hydrogen chloride.[132] Mixing basic zinc cyanurate with calcium stearate greatly promoted the thermal stability of PVC.[132] Epoxidized soybean oil improved both initial color and long-term stability.[132]

Synergistic properties of mixtures of calcium, zinc, and lanthanum salts of lanolin fatty acids have been studied.[133] Use of all three metals gave better results than usual mixture of zinc and calcium salts.[133] The optimal mass ratio was as follows: La:Ca:Zn=8:9:3.[133] Lanthanum ricinoleate alone increased onset degradation temperature and elongation and impact strength of PVC.[137]

Composition of zinc barbiturate and calcium stearate offers excellent initial color in PVC films.[134] Addition of dibenzoyl methane further improves initial color.[134] Zinc barbiturate replaces the labile chlorine atoms to interrupt the formation of conjugated double bonds in PVC chains and acts as the absorber of hydrogen chloride to restrain the self-catalytic dehydrochlorination.[134]

The non-toxic formulation of PVC containing Ca/Zn stabilizer irradiated to 75 kGy at low dose rate is more resistant to degradation than lead formulation.[135] A liquid thermal stabilizer was obtained from rosin and fatty acids.[136] The composition had excellent thermal stability.[136]

11.3.1.3 Magnesium/zinc

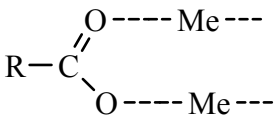
11.3.1.3.1 Properties and applications of commercial stabilizers

Table 11.5. Properties and applications of magnesium/zinc stabilizers

Chemical names: Mg/Zn carboxylate		
State: powder, liquid	**Color**: off white	**Density**, 20°C: 0.91-1.72
Exceptional properties: non-fogging, good color, low phenol, nonylphenol-free, ethylenehexanoic acid-free, butylbenzoic acid-free, compatible with PU foam backing		
PVC processing methods: coating, dip coatings, rotational molding		
Product applications: flexible to rigid PVC, carpet backing, flooring basecoat, artificial leather including automotive use, wallcoverings, gloves, conveyor bells, tamper-proof packaging		
Recommended addition rates, phr: 1 to 3		

11.3.1.3.2 Mechanisms of action

There is no information in open literature regarding the mechanism of action of Mg/Zn stabilizers. Fisch and Bacaloglu[88] analyzed FTIR spectra of different metal carboxylates and found that magnesium carboxylates are similar to lithium and aluminum carboxylates. The three carboxylates belong to a group of compounds capable of covalent bidentate bridging:



In this respect, magnesium carboxylate differs from barium and calcium carboxylates which form ionic structures. We still do not know how this difference affects stabilizing properties of magnesium carboxylate mixtures with zinc carboxylates.

Lubrication parameters have been assessed based on change of glass transition of mixtures of PVC and metal stearates. Magnesium stearate causes only small difference in glass transition temperature and because of this it is considered an external lubricant (please take note that zinc stearate is also external lubricant and both calcium and barium stearates are considered by this criterion to be internal lubricants).[88] This means that it is likely that lubrication will need to be adjusted, for example, by methyl stearate, which is an internal lubricant (as opposed to stearic acid, which is an external lubricant).

Thermal degradation kinetics, although not known from direct comparison, should be similar to Ba/Zn and Ca/Zn stabilizers.

11.3.1.3.3 Costabilizers

Thermal stabilizing composition has been patented[138] which includes zinc stearate, magnesium benzoate, and alkyl or aryl substituted β-diketone. This is similar to Ca/Zn and Ba/Zn stabilizers discussed in the previous sections. This mixture of stabilizers was developed with tamper evident packaging in mind, which requires a stabilizer with food contact properties.[138]

Other studies of different stabilizing systems led to the discovery of a system containing mixed salts of magnesium and zinc of stearic and benzoic acids, hydrotalcite, and

optionally perchlorate salt and/or β-diketone.[139] This stabilizing system gives long-term stability to products exposed to moderate temperatures, such as various internal vehicle parts which discolor on long exposures. The system has also low fogging properties and permits use of PVC articles with polyurethane foam backing.[139]

An overbased, low-fogging mixture of zinc and calcium carboxylates has already been discussed in the previous section.[114] The same method of synthesis is applied to magnesium zinc mixed overbased carboxylates.[114]

11.3.1.4 Potassium/zinc

11.3.1.4.1 Properties and applications of commercial stabilizers

Table 11.6. Properties and applications of potassium/zinc stabilizers

Manufacturers: Akcros, Baerlocher		
Commercial names: Lankromark LZK101, LZK221, LZK484, LZK506; Baerostab KK42, KK 42-1, KK 48, KK 48-1, KK 430-1,		
Chemical names: potassium/zinc carboxylates, fatty acid salts dispersion		
Ref. index: 1.45-1.51	**Density**, 20ºC: 1.02-1.18	**Viscosity**, mPas: 250-9000
State: liquid	**Color**: white	**Color (Gardner)**: 4
Composition: ethylenehexanoic acid-free, butylbenzoic acid-free; K/Zn=1:3 to 6:20		
Exceptional properties: slow to very fast kicking action, fine cell structure, resultant foam has high degree of whiteness, outstanding early color, low fogging, good heat stability		
PVC processing methods: coating, foaming		
Product applications: flexible foams, flooring, wallcoverings, coated fabrics, carpet backing, artificial leather		
Recommended addition rates, phr: 1 to 2.5		

11.3.1.4.2 Mechanisms of action

Stabilizers of fairly low thermal stabilizing performance include Zn/Cd, Zn/Pb, and Zn/K soaps. Ba/Zn, K/Zn give better thermal stability. Both groups are used as the so-called kickers; products which promote thermal decomposition of azodicarbonamide which is used in chemical foaming.

There is no preferred fatty acid for synthesizing these stabilizers, but generally they are based on synthetic fatty acids. The concentration of metals is much higher than in other liquid stabilizers. The proportion of metals also varies, but for Ba/Zn stabilizer the most typical is 3:1 and for Zn/Cd 2:1. The proportion is chosen to balance two properties: thermal stabilizing efficiency and decomposition-promoting capabilities of azodicarbonamide.

Application of both groups of stabilizers is mainly in chemically-foamed plastisols, while Ba/Zn soaps are sufficiently effective to be used as general-purpose stabilizers in everything from plastisols to rigid products. There is not much choice so far as production of low toxic materials is concerned. In such a case we have at our disposal only one kicker, K/Zn soap, as all the others are produced from highly toxic metals.

Table 11.7 shows typical data for kickers.[140]

Table 11.7. Properties of kickers. [Data from ref. (140).]

Type of kicker	Gas evolution temperature range, K	Inflection point, K
Ba/Zn liquid	398-458	403
Cd/Zn liquid	308-418	353
Ba/Cd/Zn liquid	408-463	413
Zn liquid	308-423	373
no kicker	308-483	473

The temperature range is narrower when either Ba/Zn or Ba/Cd/Zn kickers are used, while decomposition temperature is lower with Zn/Cd kicker. There is no definite answer as to which kicker is better. One group of factors is connected with formulation, the other with technological needs.

11.3.1.4.3 Research findings

A foam composition and a method of manufacture were patented.[141] Potassium and zinc activator is used in this process.

11.3.1.5 Barium/cadmium

Barium cadmium stabilizers do not play any essential role in PVC manufacturing. Cadmium-containing stabilizers were phased out in Europe in March 2001 and they are not available from any major manufacturer of stabilizers, except in the USA.[142] Long before (1983), cadmium-containing stabilizers were eliminated from medical and pharmaceutical applications.[143] Information given below has the following purposes: (a) to give an account of published research and (b) to facilitate recycling and recovery studies which have to deal with materials containing Ba/Cd stabilizers.[120,144-147]

11.3.1.5.1 Properties and applications of commercial stabilizers

Table 11.8. Properties and applications of barium/cadmium stabilizers

Chemical names: barium/cadmium carboxylate		
Mol. weight: 511-732	**Melting**, °C: 101-110	**Decomp.**, °C: 180-265
Ref. index: 1.49-1.51	**Density**, 20°C: 1.00-1.42	**State**: mostly solid
Water solubility, %: 0.004-0.008		**Solubility in solvents**, %: 0.04-0.08 (methanol)
ACGIH, mg/m^3: 0.005	**OSHA**, mg/m^3: 0.005	
Composition: Ba:Cd=2:1 to 1:2; acids C12, C14, C15, C16, C18, oleic		
Exceptional properties: eliminates plateout, high clarity, light stability		
PVC processing methods: coating, calendering, extrusion, injection molding		
Product applications: opaque articles from plasticized PVC, films, profiles, pipes, injection molded articles, window frame, sheets for outdoor use		
Recommended addition rates, phr: 0.5 to 4		

11.3.1.5.2 Mechanisms of action

Levai *et al*.[76] adapted the Debye-Hückel theory to explain the mechanism of action of Ba/Cd stabilizers. According to these findings, barium stearate, due to its greater dissociating ability, is a less effective heat stabilizer than cadmium stearate and exhibits considerably shorter induction times than cadmium stearate.

Vymazal *et al*.[148] show that acid in stabilizer affects dehydrochlorination rate. The longer the acid, the lower the dehydrochlorination rate (Figure 11.16). Branching of acid or unsaturation increases the dehydrochlorination rate. The dipole moment and polarity of carboxylates grows with the decreasing length of paraffinic chain, which explains the effect of acids on the dehydrochlorination rate. Similar results have been obtained from studies of formulations containing acids having different acid constants, pK_a. The higher the pK_a, the higher the thermostability number A (see Figure 4.71).[149] The thermostability number A is a measure of PVC thermal stability and it increases with increasing thermal stability.[150-151]

Ivan *et al*.[152] shows the effect of stabilizer concentration on induction period (Figure 11.17). These data agree with explanations by Levai *et al*.[76]

Vymazal *et al*.[148] believe that the mechanism of action of Ba/Cd stabilizers differs from Ca/Zn stabilizers because of the different position of these metals in the periodic table. They propose a mechanism other than substitution to account for the stabilizing effect of co-ordination-unsaturated metals during heat treatment of polymers. The mechanism is based on the ability of the metals to form complexes with the chlorine atoms of the

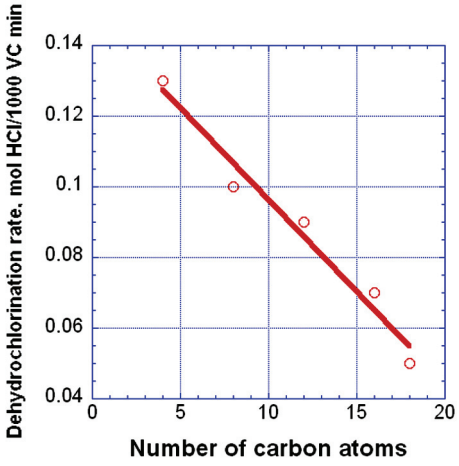


Figure 11.16. Dehydrochlorination rate of PVC containing 3.13 mol of Cd carboxylate on 1000 VC vs. the length of paraffinic chain of acid. [Data from Vymazal, Z.; Mastny, L.; Vymazalova, Z., *Eur. Polym. J.*, **25**, 10, 1069-1075, 1989.]

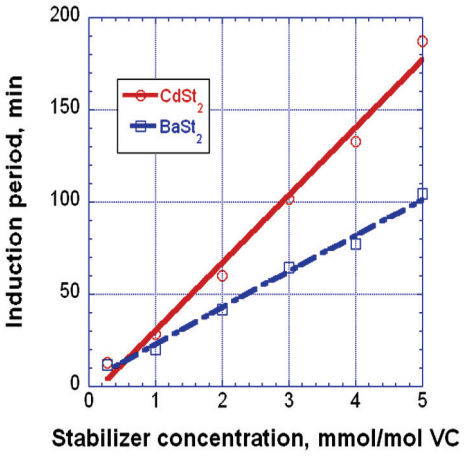


Figure 11.17. Induction period vs. concentration of stabilizer. [Data from Ivan, B.; Turcsanyi, B.; Kelen, T.; Tudos, F., *Angew. Makromol. Chem.*, **189**, 3154, 35-49, 1991.]

polymeric chain, whereby the formation of long polyene sequences, bringing about coloration of the polymer, is prevented.[148] In respect to UV stabilization, Vymazal *et al*.[153] suggest that cadmium chloride does not affect degradation rate but all damage done during processing causes formation of chromophores which affect degradation rate.

11.3.1.5.3 Costabilizers

Typical costabilizers used with Ba/Cd stabilizers are epoxy and phosphites, as well as stearic acid as an additional lubricant. The mechanism of action of epoxy stabilizers proposed by this author (see Section 11.3.1.2.3)[105] has been confirmed by Iida *et al*.[154]

Storage-stable liquid forms of Ba/Cd stabilizers were developed based on organic phosphites. Cadmium to barium proportion varies in the range of 0.5:1 to 1.5:1.[155]

Induction times were increased when Cd stearate and pentaerythritol were used together.[78] Kinetic calculations which assume the formation of a chelate formed from pentaerythritol and Cd stearate show that this chelation reduces the ionic strength of the system and thereby increases the rate of replacement of the allyl chlorines.[78] The increase in induction time is due to the reduction of ionic strength by this chelation.[78]

11.3.1.5.4 Research findings

Barium-cadmium stabilizers are mainly solid products; those which are liquid usually have phosphite added. The proportions of metals varies in the range from 2:1 to 1:2 and depends on the properties expected. For high clarity products of good early color, high cadmium stabilizers have been offered, while for long-term stability, the amount of barium was considerably increased.

The type of fatty acid used varied more in this group than in Zn/Ca soaps. Fatty acids from natural products were frequently used, including oleic acid. Synthetic acids were

also in common use. Self-lubricating properties and plateout were related to the composition of the acids used.

There was a wide variety of products in which Ba/Cd stabilizers were used – practically any product where toxicity was not a factor but, out of many applications, barium-cadmium stabilizers were particularly useful for products having high weathering resistance. By combining the effect of these stabilizers with the additional use of epoxy compounds and UV absorbers, one could further increase their weathering properties. Also, addition of phosphites was usually advisable in order to improve initial color, clarity, and outdoor stability.

Initial color was usually retained for less then 10 mins when these stabilizers were used alone at relatively low concentrations. There were three stabilizers of outstanding performance: Mark 153, Mark 426, and Therm-Chek 1827, two of which contained oleic acid. These stabilizers were sufficiently effective at low concentrations, even without the addition of secondary stabilizers.

Large amounts of PVC were processed with Ba/Cd stabilizers in the past and they are either in landfills or entering the stream of waste materials to be recycled.[120] PVC containing more than 100 mg/kg of cadmium is not permitted in a number of articles, including toys, flooring, swing doors, and other products in regular human contact.[147] In these applications post-use recyclate would need to be diluted with virgin compound or post-industrial recyclate.[147] There are many other applications including windows, drainage pipes, structural products, etc., where there is no restriction on the cadmium content from recyclate.[147] A technological process is also available, which permits conversion of PVC metal stabilizers to metal chlorides, following their removal from PVC waste before it is converted into usable articles.[144]

11.3.1.6 Barium/cadmium/zinc

Similar to Ba/Cd stabilizers, these stabilizers lost most of their applications because of cadmium toxicity.

11.3.1.6.1 Properties and applications of commercial stabilizers

Table 11.9. Properties and applications of barium/cadmium/zinc stabilizers

Past manufacturers: Akcros (US), Ferro			
Commercial names: Acrostab BC-103A, BC-103A EXP, BC-111, BC-4746S; Lankromark LC486LO, LC541; Therm-Check MX 125, SP 1797			
Chemical names: barium/cadmium/zinc carboxylate			
Mol. weight: 464-732	**Melting**, ^{o}C: 70-183	**Decomp.**, ^{o}C: 180-265	**Flash point,** ^{o}C: 60
Ref. index: 1.47-1.51	**Density**, 20^{o}C: 0.91-1.09	**Viscosity**, mPas: 6-1850	
Water solubility, %: 0.001-0.008		**Solubility in solvents**, %: 0.003-0.084 (methanol)	
State: liquid	**Color**: amber	**ACGIH**, mg/m^3: 0.01	**OSHA**, mg/m^3: 0.5
Composition: Ba:Cd:Zn=10:6:1 to 10:12:1 to 10:7:4 to 4:6:1; acids: C8, C9, C12, C13, C15, C16, C18, oleic			
Exceptional properties: minimal plateout, low color, light stability, air release, kicker			
PVC processing methods: knife, reverse-roll, calendering, extruded and closed mold processes			
Product applications: all-purpose, film, flooring, printed fabrics, gloves, profiles, sheet			
Recommended addition rates, phr: 0.8 to 4			

11.3.1.6.2 Mechanisms of action

There is no evaluation of the mechanism in the available literature. It has to be assumed that the mechanism is a combination of the mechanism of Ba/Zn and Ba/Cd stabilizers.

11.3.1.6.3 Costabilizers

Epoxy, UV, and phosphite have been suggested for many stabilizers as suitable costabilizers. Epoxy costabilizers were used in all applications. Lubrication was sufficient in many instances. Only in some cases, additional stearic acid has been suggested.

11.3.1.6.4 Research findings

Unlike Ba/Cd soaps, most of the products included in this group were liquid stabilizers. The average concentration of active component (primary stabilizer) was about 50%; the remaining part was a solvent, in most cases phosphite. This was why the addition of phosphite was usually not suggested. The proportion of metals varied less than in Ba/Cd stabilizers. The major group consisted of products in which the total concentration of zinc and cadmium was equal that of barium. Again, in this case the concentration of metals was varied in order to obtain the expected balance between clarity, initial color, and long-term thermal stability. Additionally, the increased zinc was meant to deter sulfide-staining.

Acids having C15 and C12 were the most common. The inclusion of a longer fatty acid chain (e.g., stearic acid) improves lubrication and allows to take advantage of the unknown mechanism by which stearic acid improves initial color, long-term stability, and plateout. Especially in products which do not contain this acid, it is advisable to add it as a lubricating agent. An unusual composition was exhibited by the only kicker included in this group that appeared to be like two kickers, Zn/Cd and Ba/Zn combined.

The big difference in viscosity among stabilizers in this group is surprising, as there is no apparent reason for it.

The thermal stability of products was predictably high. Usually one could observe evaporation of solvent, which should had no impact on product quality, since stabilizers were added in small quantities, and these "solvents" were not very volatile.

Stabilizers in this group are mainly used in semi-rigid PVC and plastisols. In the case of plastisols, they usually help in deaerating the pastes, which was a time-saving property, essential in industrial practice. They are known for good efficiency and long-term stability, and they give light-fastness to final products. Their ability to form transparent plastificates is one of their essential features. Furthermore, these stabilizers are compatible with plasticizers, because of the type of solvents used in their preparation. Their main disadvantage is the toxicity of the metals used, and in some cases, sensitivity to temperatures of storage and transportation.

IR and UV spectra are very helpful in recognizing the addition of phosphite. It can be immediately spotted by the presence of a sharp peak at 1580 cm^{-1}. Small double peaks between 3100 and 3000 cm^{-1} show the presence of aromatic rings in phosphites, as does absorption below 230 nm on the UV spectrum. Liquid Ba/Cd/Zn stabilizers usually contain phosphite having aromatic ring(s).

When these stabilizers are used, color stability is definitely better than with Ba/Cd soaps. It is evident that by increasing the participation of group IIb metals, better initial color and worse long-term stability are achieved, which is not so easily seen when these changes are smaller. Overall enhanced color stabilization should not be attributed to the metal composition alone, but it is a combined effect influenced by phosphite in the stabilizer.

11.3.1.7 Lanthanum soaps

The lanthanum ricinoleate can be synthesized by the reaction of ricinoleic acid, lanthanum nitrate and sodium hydroxide.[137] Together with pentaerythritol (3 parts per 1 part of soap) it forms a synergistic mixture.[137] This stabilizer improves maximum and onset degradation temperature as well as elongation and impact strength of PVC.[137] It may replace the labile chlorine atoms to interrupt the formation of conjugated double bonds and act as HCl scavenger.[137] In comparative study, it performed better that lead and organotin stabilizers.[137]

Lanthanum stearate was studied as a costabilizer of calcium stearate/zinc glutarate.[156] Substantial improvement of stabilization efficiency to PVC compared with the Ca/Zn stabilizers was observed.[156]

11.3.2 LEAD STABILIZERS

Lead stabilizers have served the PVC industry with very efficient stabilization of some major products such as wire and cable, window profiles, water pipe, etc. In the 1970s this author developed a formulation to replace lead stabilizers in wire and cable by a more efficient formulation but industry then was not ready to accept any alternative solutions. Their excellent performance discouraged any potential attempts to replace them until it became evident that health and safety hazards override their performance and these stabilizers are now under strong scrutiny. The European Commission Green Paper has highlighted concerns about the continued use of lead stabilizers.[142] A resolution from the European Parliament[157] on the Green Paper stated that lead stabilizers should be phased out, but did not indicate a specific timetable.[142] Some member states have already implemented a lead phase-out policy (Sweden and Denmark banned virtually all products containing lead).[159] The European Community Directive on drinking water quality[158] long ago highlighted that lead stabilizer would not be approved for use in PVC pipes after 2003.

Because of the voluntary commitment of the PVC industry to replace lead-based stabilizers before the end of 2015, their use is decreasing fast.[193] The use of lead and its compounds is also restricted by EU legislation through the RoHS Directive, the Packaging Directive and the ELV Directive.[193] Lead and many lead-containing substances have recently been included in the REACH Candidate List.[193] All these developments affect not only the use of lead stabilizers but also future recycling of PVC materials.[193]

In North America, unlike in Europe, window and door profiles were stabilized with tin stabilizers. The major use of lead stabilizers is in wire and cable. Wire and cable industry is changing its stabilizers to Ca/Zn. Halstab (the major manufacturer of lead stabilizers) announced availability of alternative stabilizers for wire and cable and offers help in replacement. The current manufacturer of Halstab stabilizers – AM Stabilizers – does not use lead and cadmium in any of their products.

It should be pointed out that studies have confirmed that lead stabilizers are absorbed into the polymer matrix and that they do not migrate from the plastic. The leachability of lead from PVC is extremely low. The amount of lead extracted from lead-stabilized water pipes is negligible. The encapsulation immobilizes the lead stabilizer and prevents it from entering the environment. The situation is less clear when PVC is finely divided. Waste products such as cable fluff or granulated profiles have increased surface area which may facilitate extraction in the presence of acidic landfill leachates.

11.3.2.1 Properties and applications of commercial stabilizers

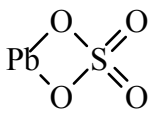
Table 11.10. Properties and applications of lead stabilizers

Manufacturers: Baerlocher, Addenda			
Commercial names: Baerostab V MC 220, V MC 420, Pebetal, PB 51 S, Pb 28 f, Pebefos FP, Pebefos; add-iBase, addiBase PG			
Chemical names: dibasic lead phthalate, dibasic lead stearate, dibasic lead phosphite, dibasic lead phosphite/sulfite, lead oxide sulfate, neutral lead stearate, tetrabasic lead sulfate, tetrabasic lead fumarate, tribasic lead maleate, tribasic lead sulfate			
CAS#: 1072-35-1, 12036-76-9, 12141-20-7, 12202-17-4, 12275-07-9, 12578-12-0, 13698-55-0, 52732-72-6, 69011-06-9		**EC#**: 214-005-2, 234-853-7, 235-252-2, 235-380-9, 235-702-8, 258-142-6, 265-549-7, 235-702-8, 237-220-3, 258-142-6, 273-688-5	
Mol. weight: 743-1220	**Melting**, ºC: 110-250	**Density**, 20ºC: 1.4-7.2	**State**: powder
Color: white to cream	**Odor**: odorless	**Density**, 20ºC: 1.4-7.2	**ACGIH**, mg/m^3: 0.05
OSHA, mg/m^3: 0.05		**LD50, rat**, mg/kg: 2000-15000	
Composition: Pb: 27 to 83%			
Exceptional properties: electrical properties, long-term stability, low solubility in water, does (or does not) delay fusion, antioxidant properties			
PVC processing methods: calendering, extrusion, injection molding			
Product applications: flexible to rigid PVC, profiles, wire and cable, water pipe, film, sheeting, garden hose			
Recommended addition rates, phr: 0.5 to 2			

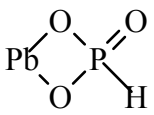
11.3.2.2 Mechanisms of action

Lead has properties similar to tin, which is in the same group of the Periodic Table. Like tin, lead can exhibit a positive valence of two or four, and, additionally, but very seldom, of one or three. In common thermal stabilizers, lead, unlike tin, is bivalent.

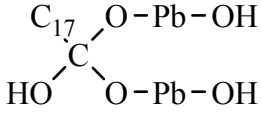
Lead oxide, which is included in most lead stabilizers, is the main stabilizing component that is able to react efficiently with hydrogen chloride. Lead oxide is structurally bound to lead salts of some organic and inorganic acids, such as stearic, maleic, phthalic, fumaric, salicylic, carbonic, silicic, sulfuric, and phosphoric acids. Maleic and phthalic acids offer structures similar to those of some organotins. Stearic acid forms a compound identical to metal soap stabilizers, whereas phosphite can resemble an inorganic variety of organic phosphites. Other compounds are typically inorganic materials. The following chemical formulas characterize various lead stabilizers:[160,161]



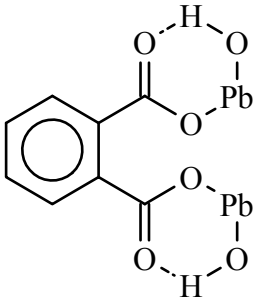
normal lead sulfate



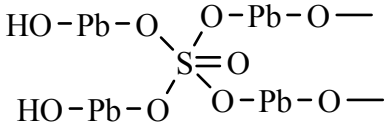
normal lead phosphite



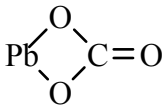
dibasic lead stearate



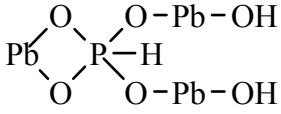
monobasic lead phthalate



tribasic lead sulfate



normal lead carbonate



dibasic lead phosphite

From this brief comparison, lead stabilizers may be viewed as complete system which permits the creation of synergistic compositions (based on lead compounds) because of the diversity of forms available. The manufacturing methods are flexible enough to obtain mixtures of components in which differences in the mechanisms of action can be exploited.

Comparing the reactivity of basic lead sulfate, lead oxide, and lead sulfate with HCl, Zilberman[162] found that the basic salt was the most reactive of the three. Lead sulfate may react with hydrochloric acid, but the yield of lead chloride is rather low. Michel[163] studied the reaction between HCl and white lead in diethylhexyl phthalate suspension and found that reaction proceeds through intermediates; he reached the same conclusion from studies on polymer blends.[164] These studies were repeated later for lead carbonate and white lead by Ball,[165] who showed that lead chloride, formed in a single stage, is the only product of the reaction. X-ray diffraction analysis showed that under any reaction conditions the only product formed was lead chloride, with no evidence of intermediates. Reactions occurred according to equations:

$$PbCO_3 + 2HCl \longrightarrow PbCl_2 + CO_2 + H_2O$$

$$2PbCO_3 \cdot PbO \cdot H_2O + 6HCl \longrightarrow 3PbCl_2 + CO_2 + 4H_2O$$

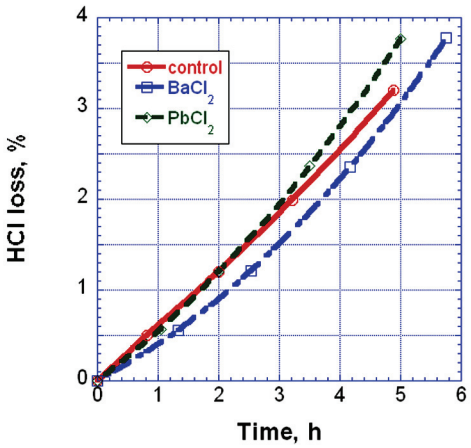


Figure 11.18. The effect of some metal chlorides on PVC thermal dehydrochlorination at 448K (5 mmol of metal chloride per 100 g of PVC). [Data from Wirth, H. O.; Andreas, H., *Pure Appl. Chem*., **49**, 627, 1977.]

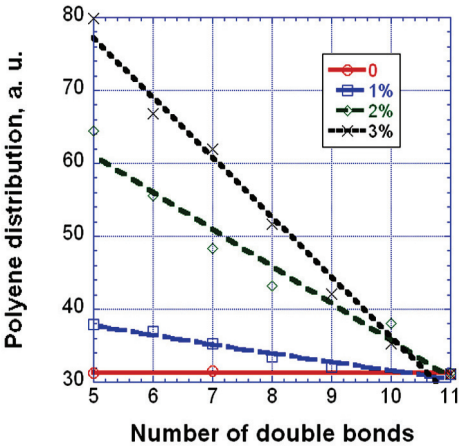


Figure 11.19. Polyene length distribution in degraded PVC stabilized with varying concentrations of lead octoate (degradation for 1 hr at 453K). [Data from Braun, D.; Hepp, D., *Angew. Makromol. Chem*., **66**, 23, 1978.]

The activation energy was seven times higher for lead carbonate than for white lead. The rate of reaction is controlled by the HCl diffusion rate.

According to Wirth,[166] bivalent lead possesses the chemical properties needed to replace labile chlorine atoms. Figure 11.18 shows that lead chloride practically does not influence the rate of PVC dehydrochlorination, which is similar to that of PVC alone or to PVC containing barium chloride.

The distribution of the length of polyene sequences depends, according to Braun,[167] upon the amount of lead octoate (Figure 11.19).

Minsker[168] observed that salts of stearic and lauric acids decreased polyene growth, and that the type of acid also had an effect on the process and dehydrochlorination kinetics. Basic salts of lead may form complexes with partially dehydrochlorinated PVC which retards the initial color.[162,169,170] The other explanation of color retardation which has been given involves the oxidation of conjugated double bonds.[170-172] Wypych[173] noted that, in the presence of dibasic lead stearate and tribasic lead sulfate, the crosslinking reaction occurred. These reactions may also contribute to color retardation.

According to Minsker,[174] lead stabilizers, based on their thermostabilizing activity, can be arranged into the following order: lead stearate > dibasic lead phthalate > dibasic lead stearate> dibasic lead phosphite > tribasic lead sulfate.

Moritz's paper[175] contains interesting data on possible reactions of lead stabilizers with carbon dioxide, which can be explained by the following equations:

$$PbHPO_3 \cdot 2PbO \cdot 1/2H_2O + 2CO_2 \longrightarrow PbHPO_3 \cdot 2PbCO_3 \cdot 1/2H_2O$$

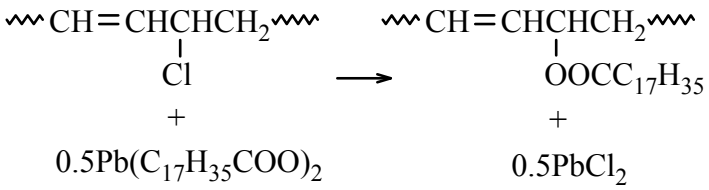
$$Pb(C_{17}H_{35}COO)_2 \cdot 2PbO + 2CO_2 \longrightarrow Pb(C_{17}H_{35}COO)_2 \cdot 2PbCO_3$$

Finally, it is important to mention an early observation[176] that lead oxide is able to react with stearic acid as follows:

$$2PbO + 2C_{17}H_{35}COOH \longrightarrow PbO \cdot Pb(OOCC_{17}H_{35})_2 + H_2O$$

Stearic acid is usually present in PVC compositions, as it is frequently used as a lubricant. One may predict, therefore, *in situ* formation of another stabilizing component or its recovery, if it was initially present.

Michell[178] extended the above mechanisms to include substitution of acid rests into to the polymers chain. According to his mechanism, aliphatic carboxylate groups (such as the stearate ion) react with basic lead compounds (such as white lead) to form salts. These salts react with chlorine atoms released by the PVC during its decomposition, to give chlorides of lead and the aliphatic carboxylate free radicals. The aliphatic carboxylate free radicals can esterify PVC chains at sites where chlorine atoms have abstracted methylenic hydrogen leaving unpaired electrons. This step interferes with the free radical propagation mechanism and lowers the overall degradation rate. The above mechanism of substitution can be expressed by the following equation:[178]



Thermogravimetric analysis of PVC degradation shows that more HCl is lost without stabilizer than in the presence of lead decanoate.[179]

Table 11.11 gives data on the lead content in lead stabilizers compiled by AKZO.[177]

Table 11.11. Lead content in main lead stabilizers. Data from Ref. 177.

Formula	Lead content (% w/w)		
	Total	Reactive	Uncombined
$Pb(OH)_2 \cdot 2PbCO_3$	80.2	80.2	26.7
$2PbO.PbCO_3$	87.1	87.1	58.1
$3PbO.PbSO_4 \cdot H_2O$	83.6	62.8	62.8
$2PbO.PbHPO_3 \cdot 1/2H_2O$	83.7	83.7	55.8
$2PbO.(C_{17}H_{35}COO)_2Pb$	51.0	51.0	34.0
$(C_{17}H_{35}COO)_2Pb$	27.0	27.0	0.00
2PbO.Pb phthalate	76.0	76.0	50.6
$3PbO.Pb\ maleate.H_2O$	82.1	82.1	61.6

Except for tribasic lead sulfate, all stabilizers contain metal that can be completely converted into lead chloride. Even lead sulfate can be partially reacted, but it would produce a strong acid that would affect the degradation rate; therefore, under practical conditions this stage is never achieved.

The last row of values contains data on the contents of material that can be converted into lead chloride without producing residual acid. It is customary to use only that part of the stabilizer in the case of lead compounds containing inorganic acids (except phosphite). These findings contradict Ball's results[165] mentioned earlier, but seem to agree with practical observations. For example, in the case of basic lead carbonate, it is not advisable to use the stabilizer as intensive gassing occurs, which affects the quality of the material.

Concerning inorganic materials included in this group, one can say that the main role they fulfill is to react with HCl that is evolved. It is not possible for them to substitute any acid residue into the polymer chain. These stabilizers resemble metal soaps containing calcium or barium, which means they are HCl acceptors but, at the same time, they are able to stabilize color, which carboxylates cannot do.

As can be seen from the above literature survey, the phenomenon of color stabilization cannot be fully explained, but the most probable reasons for it is either complex formation with a conjugated double-bond system or participation in a crosslinking reaction. No matter what the true reason, the phenomenon deserves further study since it might be proven that the nature of the metal rather than the other constituents of the stabilizer molecule determines color stabilization. In such a case, the elaborate theory of stabilization by metal soaps may prove invalid. If not, it means that lead stearates take part in PVC stabilization in the same manner as metal soaps (as proposed by Michell),[178] which means they are able to substitute labile chlorine atoms by introducing into the polymer chain the acid groups through which the polyene sequences are shortened. Apart from this, they are HCl acceptors and good lubricants, whereas inorganic lead stabilizers have no lubricating properties. The lubricating properties of lead stearates are probably the main reason for their use in industrial processes. They are seldom used alone as excessive amounts of stearic acid may exude from some compositions.

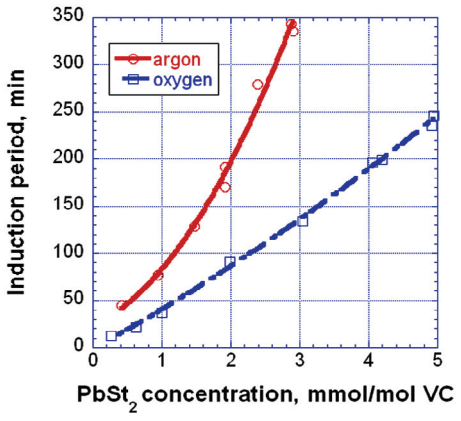


Figure 11.20. Induction period vs. $PbSt_2$ concentration during degradation in argon and oxygen. [Data from Ivan, B.; Turcsanyi, B.; Kelen, T.; Tudos, F., *Angew. Makromol. Chem.*, **189**, 3154, 35-49, 1991.]

Figure 11.20 shows that the induction periods at the same stabilizer concentrations are significantly shorter during thermooxidative degradation than under inert atmosphere. The overall rate of dehydrochlorination is markedly higher under thermooxidative conditions than under inert atmosphere in the presence of lead stabilizers.

Dibasic lead phosphite, like organic phosphites, should be able to react with HCl, complex metal chlorides, and interact with other stabilizers. This is probably why dibasic lead phosphite is always used when good outdoor properties are needed. The function of phosphite is, therefore, not only to accept HCl but also to affect initiation of dehydrochlorination and to react with peroxides.

Tribasic lead maleate, similar to tin maleates, can improve color as a result of a Diels-Alder reaction.

Dibasic lead phthalate is known for its excellent electrical properties; therefore, in spite of its relatively high price, it was frequently used in the cable industry. All lead stabilizers exhibit good electrical insulating properties, which in this case, are attributable to the special properties of lead chloride.

Lead stabilizers were found to participate in the so-called pinking mechanism which leads to discoloration of PVC windows (more on this mechanism in Section 11.3.5.2).[180] A study was devoted to explanation of the role which the lead stabilizers may play in pink discoloration but it was only found that addition of trace lead oxides accelerates pinking, whereas some titanium dioxide grades reduced it.[194] It was also suggested that a redox reaction between the titanium dioxide and the lead stabilizer that may facilitate the production of short polyene chains in the PVC matrix producing the pink coloration.[194]

11.3.2.3 Costabilizers

Costabilization of lead stabilizers is a part of their production processes as discussed below.

Traditionally, these stabilizers were produced by the so-called "wet method," in which lead monoxide (litharge) was reacted with a particular acid in an aqueous medium in the presence of a catalyst, usually acetic acid. The catalyst was needed because of the low solubility of litharge in the reacting mixture. This method has several inconvenient consequences. First, soluble lead acetate is formed from the reaction, and it cannot be left in the main component as it would affect the quality of the stabilizer. Therefore, the product has to be carefully washed, which means lead loss, production of waste water containing a dangerous chemical substance, and additional costs in manufacturing of a stabilizer which is supposed to be very cheap. Secondly, lead monoxide used in this process is produced in accordance with technology which allows formation of crystalline forms responsible for the initial color of the resulting stabilizer. Litharge also contains admixtures of Pb_2O_3 and PbO_2, retained after salt is produced, which affect the color of stabilizers. Finally, stabilizers produced by this process are in a powder form of particle size distribution insufficient to enhance their dispersibility in polymer mixtures, but sufficiently fine to cause health hazards in manufacturing and processing.

When this technology was the only one available, the typical formulation for outdoor application had to include at least three stabilizing components: basic lead sulfate as a source of HCl-accepting power, basic lead phosphite to combine thermostabilizing action with aging properties, and lead stearate to achieve proper lubricating properties. As the lubrication was never properly adjusted with a single component, other lubricants were also included. All components were to be weighed and incorporated properly, usually in large amounts.

As a result of these complications, research was in progress in the 1960's in order to find another solution. By the end of that decade a solution was found by an AKZO team that succeeded in preparing lead stabilizers in a new form based on an entirely different principle. The new products, called coprecipitates, are most probably produced according to the technology discussed in the patent.[181]

The purpose of the research was to provide a dust-free lead stabilizer. As in most cases, lead stabilizers cannot be dissolved, which would resolve the problem. Instead, stabilizers were tried in the form of pastes with, for instance, plasticizers, but here again the physical properties were not helpful as lead products are of a very high density as compared with potential liquids used for dispersion; therefore, stable pastes were not obtained. The technological process mentioned in the above patent[181] concerns the mixture of basic lead salts with an ester wax or high molecular weight alcohol with an alternative addition of metal soaps. The stabilizer mixture is produced *in situ* by incorporation of calcium oxide into molten spermaceti, tallow alcohol, stearic acid, stearyl alcohol, and so on. After calcium oxide has reacted, the lead salt or oxide is introduced, and shortly after being reacted, the mixture is flaked by a cooling roller or formed by extrusion.

There are a number of options in this process, as all the mixture components are able to react with each other; therefore, when, for example, tetrabasic lead sulfate is introduced into the mixture containing stearic acid, substantial amounts of lead stearate are produced. By varying the proportions of components and reaction conditions, one can obtain different products. For instance, soap formation in the melt can be facilitated by adding a small amount of water, acetic, or formic acid. The reaction between calcium stearate and basic lead sulfate can be stopped by adding a lubricant to the melt; therefore, one can also produce a stabilizer that retains the initial properties of the substrates used. It is important to note that the final mixture obtained in this process is more effective than it would have been if all the components were mechanically mixed together, which is attributable to their synergetic effect.

In another source[182] one also finds a method for combining lead salts with lubricant to form a novel product. Here compositions of lead salt with partial esters of pentaerythritol are discussed. It is demonstrated that the presence of lubricating agent may enhance the performance of lead stabilizer and improve the initial color of the composition. In some cases stabilizer effectiveness was increased by a factor of four.

The author of another patent[183] argues that, because the lead attached to inorganic acid residue is inactive in the stabilizing process, it causes substantial loss of lead (25-33%). This author contends that binary adducts with pentaerythritol are far more effective. The product can be obtained in single batch processes in composition with other stabilizers such as lead stearate, cadmium stearate, and so on.

Still another patent[184] resolves the problems of the production of lead monoxide and related lead salts used in stabilization by the modernized technology of the wet process. By controlling both the pH value at the initial stage of reaction and the presence of hydroxylamine, lead monoxide of an entirely different crystalline structure is obtained. The lead monoxide can be reacted with any mineral or organic acid without acetic acid being present, and the resulting product is not colored by oxides of higher lead valence.

Additionally, it is possible to obtain tribasic lead sulfate of such fine particles that transparent PVC products can be produced.

The performance of these stabilizers has improved due to the synergism of their components' action, and for this reason they can be applied where limits are imposed on the lead concentration in the final product, as, for example, in the case of pipes for potable water.

All these stabilizers have a low melting point, because of the organic part that is included in their technology of production. A low melting point is essential for their compounding. The producer always emphasizes that these stabilizers are to be incorporated into the polymer mass by a dry blending process at 383K, and a low melting point facilitates the mixing procedure as well as the distribution of stabilizer in the polymer.

Stabilizer density correlates with metal concentration and it is an important factor characterizing lead stabilizers. IR spectroscopy conveniently distinguishes between sulfates, phosphites, and phthalates of lead. Phosphites have a characteristic band at 550 cm^{-1} which neither of the other groups has. Phthalates can be recognized by specific bands between 650 and 850 cm^{-1} which are also not present in the spectra of the other two groups. By contrast, IR spectroscopy has little value for the identification of lubricants because they are present in the mixture in small amounts, insufficient for identification.

11.3.2.4 Research findings

Traditionally, the main application of lead stabilizers has been in the cable industry because of their high volumetric resistivity, which is well characterized by data in Table 11.12.

Table 11.12. Volumetric resistivity of PVC plastificates containing various lead stabilizers (PVC-100, DOP-50, stabilizer-5 parts). [Data from Ref. 184.]

Lead stabilizer	Volumetric resistivity x 10,000 Mohm cm
tribasic lead sulfate	1.8
tetrabasic lead sulfate	5.5
tribasic lead phosphite	5.5
lead phthalate	0.8
dibasic lead stearate	0.7

Stabilizers for the cable industry usually have the highest concentration of metal, accompanied by a low internal and medium external lubrication. In a stabilizer meant for thin-wall cables, external lubrication is increased.

High voltage cable insulation was electrically aged (18 years outdoors at 6±10 kV).[185] Only 2 wt% of plasticizer was lost and the remaining plasticizer was unchanged. 20 wt% of Pb-based stabilizer system was found in the non-active form; no loss of filler occurred during the service life of the PVC electrical cable insulation waste.

Figure 11.21 shows that window profile stabilizer (Pb/Ba/Cd) gives worse performance than Ca/Zn carboxylate stabilizer. Photooxidation occurs faster in the presence of lead-containing stabilizer.[186] Ca/Zn stabilizers provided window profiles with better color retention than Pb/Ba/Cd stabilizers.[186] When Ca/Zn stabilizers in PVC are exchanged for

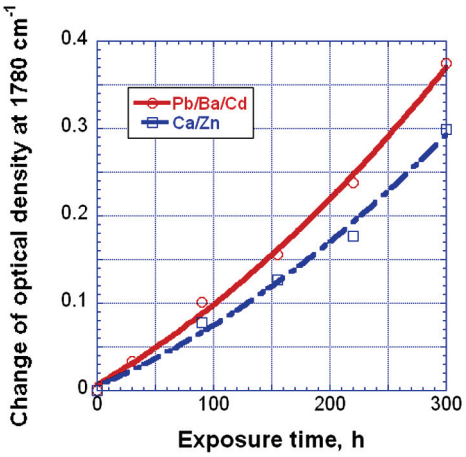


Figure 11.21. Photooxidation of PVC profiles containing Pb/Ba/Cd and Ca/Zn stabilizers. [Data from Gervat, L.; Morel, P., *J. Vinyl Additive Technol.*, **2**, 1, 37-43, 1996.]

Pb stabilizers, gloss degradation rate doubles.[187]

Many vinyl miniblinds have been found with surface lead exceeding 0.1-0.2 μm/cm^2.[188] Levels of 1-10 μm/cm^2 are common, with some specimens as high as 40-80 μm/cm^2. These concentrations are found after UV exposure of miniblinds. It was suggested that some of this lead content may be due to conversion of lead dust in air to chlorides.[188] This explanation seems unlikely (it is rather the process of deterioration under UV), although the explanation is less important because what matters most is the concentration of lead, weakly attached, which can be easily transferred to human skin. Because of potential danger of contamination, the US Window Covering Safety Council announced voluntary elimination of use of lead stabilizers in vinyl miniblinds.[189]

The other major group of products includes stabilizers for production of rigid pipes by twin-screw extruders. These usually have medium lubricating properties and are used in amounts of 1-2 phr. They are usually of low metal content, and the least concentrated are applied in the production of pipes for potable water in order to comply with safety regulations.

Leaching of lead is still a matter of controversy partially caused by testing methods.[190] The result frequently depends on extraction conditions but also on conditions of extrusion.[190]

The above review and toxicity of lead discussed in Chapter 12 caused extensive changes in use of stabilizers and voluntary and compulsory elimination of leads stabilizers. This raises the question of PVC recycling which may contain lead stabilizers. One basic problem always to be considered is that lead stabilizers and tin stabilizer may react, forming dark spots of lead sulfide in the recycled material.[120] This potentially catastrophic effect has to be accounted for in recycling procedures by inclusion of proper testing procedures.

Recycling of a single source (containing only lead stabilizers) is usually very simple since it frequently does not require additional stabilization because of excellent long-term performance of lead stabilizers.[191] In this respect, lead stabilizers are superior to any replacement stabilizers. At the same time, future regulations must be considered. If future regulations will establish reasonable residual concentrations, then wastes can be compounded with lead-free PVC to dilute lead to acceptable concentrations.

The other option includes chemical recycling in which $PbCl_2$ is removed.[144] The process is based on a combined thermal and chemical degradation of PVC in a reactor. The

metal stabilizers (lead, cadmium, zinc and/or barium) are converted to metal chlorides.[144] The other process proposed for such application is steam gasification which converts of about 70% carbon to gas at 1150K.[192] This shows that there is no simple solution for the processing of future wastes.

11.3.3 INORGANIC STABILIZERS

Hydrotalcite, modified zeolite and montmorillonite are effective stabilizers of PVC compositions.[195-205]

11.3.3.1 Properties and applications of commercial stabilizers

Table 11.13. Properties and applications of inorganic stabilizers.

Manufacturers: Clariant, Kisuma, Nabaltec AG			
Commercial names: Sorbacid, Alcamizer, Actilox CAHC			
Chemical names: hydrotalcite (synthetic magnesium-aluminium-hydrotalcite or magnesium-aluminium-zinc-hydrotalcite), zeolite, hexadecyltrimethylammonium bromide modified montmorillonite, calcium-aluminium double hydrate			
CAS#: 11097-59-9		**EC#**: 234-319-3	
Mol. weight: 603.98	**Melting**, °C: >250	**Density**, 20°C: 2.03-2.2	**State**: powder
Color: white (brownish)	**Odor**: none	**Ref. index**, 20°C: 1.495-1.529	
Composition: $Mg_6Al_2CO_3(OH)_{16}$ $4(H_2O)$			
Exceptional properties: environmentally friendly, non-toxic and heavy metal-free, flame retardant, smoke suppressant			
PVC processing methods: flexible, rigid, transparent			
Product applications: window profiles, cables, coated wires, pipes			
Dose: wt%: 1-3			

11.3.3.2 Mechanisms of action

Cations of the hydrotalcite structure influence how hydrotalcite works as an anion-exchanger and why it is used as a halogen-scavenger in PVC.[202] The ionic radius of Mg^{2+} is 0.072nm and that of Ca^{2+} is 0.100 nm.[202] Because of the smaller ionic radius of Mg^{2+} more ions per unit area are available, thus binding more HCl gas molecules and giving more stabilization power to Mg-Al-OH-X hydrotalcites.[202] The HCl evolution depends on the rate of dehydrochlorination but color depends on the length of polyenes formed.[203] Adsorption and ion exchange are responsible for action of hydrotalcites as long-term stabilizers.[203]

Hydrotalcite improves the long-term stability of PVC and inhibits crosslinking.[204] X-ray diffraction measurements show that there is some exfoliation of the hydrotalcite layered structure, followed by intercalation.[204] This means that the PVC chains separate the hydrotalcite layers. It is anticipated that this prevents formation of crosslinks.[204]

11.3.3.3 Costabilizers

β-diketones were found to be suitable costabilizers for metal soaps and hydrotalcide combinations.[203]

Hydrotalcite improved performance of tin stabilizer.[205] Increased content of hydrotalcite causes increase in thermal stabilization by two stabilizers.[205]

11.3.2.4 Research findings

$MgAlCe\text{-}CO_3$ layered double hydroxides were investigated as PVC thermal stabilizers.[195] The thermal stability time was 190 min when 3 phr were added as sole stabilizer.[195] Layered double hydroxide formed synergistic mixtures with zinc and calcium stearates.[195]

Zn-Al-La hydrotalcite-like compounds were used as thermal stabilizer of PVC resin.[197] They also belong to layered double hydroxides.[197] This stabilizer used as single thermal stabilizer enhanced both the long-term and initial thermal stability of PVC.[197]

The zeolite was found to be the most effective stabilizer for PVC as compared with hexadecyltrimethylammonium bromide modified montmorillonite and 3-aminopropyltriethoxysilane-grafted montmorillonite.[200]

Synergistic stabilizing effect of layered double hydroxides with nano-sized calcium carbonate on thermal stability of polyvinyl chloride was observed.[201]

11.3.4 ORGANOTIN STABILIZERS

Organotin stabilizers are purely synthetic products; therefore, the major consideration is to use common raw materials, which are the most economically feasible. There are four main reasons for a choice of a particular compound for industrial production of organotin stabilizer: cost and availability of raw materials; effectiveness in thermal stabilization; post-processing characteristics (protection against weathering, etc.); and toxicity of stabilizer and/or its reaction products.

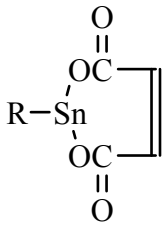
Based on the above criteria, many potential stabilizing components were synthesized; 40 years ago their number was estimated to be over one thousand,[206] and it may now be assumed to reach several thousand. Organotin stabilizers have been reviewed in detailed papers.[166,206-216] Organotin stabilizers can be classified as follows:

1. Carboxylate derivatives.

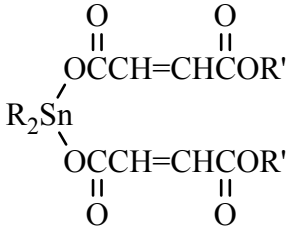
(a) Dialkyltin dicarboxylate:

$$R_2Sn(OOCR')_2$$

(b) Dialkyltin maleate:

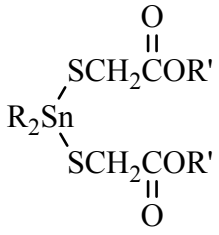


(c) Dialkyltin bis(ester maleate):

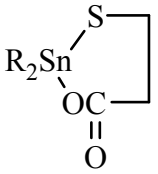


2. Sulfur-containing organotins.

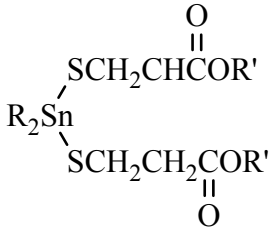
(a) Dialkyltin bis(ester thioglycollate):



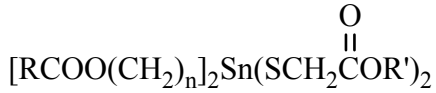
(b) Dialkyltin β-mercaptopropionate:



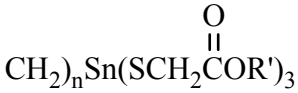
(c) Dialkyltin bis(ester mercaptopropionate):



(d) Diestertin bis(ester thioglycollate):



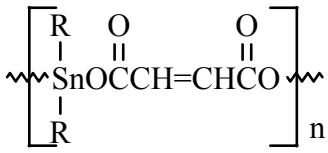
(e) Estertin tris(ester thioglycollate):



3. Carboxylate-mercaptides.

4. Polymeric stabilizers.

(a) Polymeric organotin stabilizers:[216-219]



(b) Polymers of vinyltin compounds,[220,221]

(c) Polymers of other unsaturated organotin compounds.[222-225]

The above list does not include the full variety of components described in the literature as potential PVC stabilizers. There are some known derivatives containing other metals, such as zinc,[226] antimony,[227] and boron.[228,229] Carboxylic acid usually has a short chain, but some products are reported to have carboxylic acids of high molecular weight.[230,231] In a very detailed discussion of tin stabilizers,[206] one can find still other products thought to be effective PVC stabilizers. The industrially important compounds are only a small fraction of those discussed in the literature and patented.

Based on the above breakdown, some of the most typical (dialkyl) organotins have been chosen in order to illustrate their basic physical properties. The data are included in Table 11.14.

Table 11.14. Basic properties of selected tin stabilizers.

Name	MW	Sn, %	MP, K	DP, K	RI
Bu_2Sn dilaurate	631.55	18.8	300	>513	1.467
Oct_2Sn dilaurate	743.77	16.0		>513	1.469
Bu_2Sn maleate	346.98	34.2	383	>513	
Oct_2Sn maleate	459.19	25.8	353	>513	
Bu_2Sn bis(isooctylmaleate)	687.47	17.3		>513	1.483
Me_2Sn bis(isooctylthioglycollate)	551.38	21.5		>513	1.506
Bu_2Sn bis(isooctylthioglycollate)	639.57	18.6		>513	
Oct_2Sn bis(isooctylthioglycollate)	751.79	15.8		>513	1.498
Bu_2Sn β-mercaptopropionate	337.05	35.2	394	>513	
Bu_2Sn bis(isooctylthiopropionate)	667.62	17.8		>513	1.491
Bu_2Sn bisthiododecane	635.71	18.7		>513	1.498

Me – methyl, Bu – butyl, Oct – octyl, MW – molecular weight, Sn – tin concentration, MP – melting point, DP – decomposition point, RI – refraction index.

Organotin compounds exhibit very good thermal properties; their decomposition temperatures are far above the temperatures of PVC processing. The melting point of some organotins is sufficiently low that they may solidify under normal weather conditions in many countries.

From this list one can see that, depending on chemical composition, stabilizers contain a tin concentration that varies widely; for example, dibutyltin maleate contains more than double the amount of tin as compared with dioctyltin bis(iso-octyl thioglycollate). As the amount of tin determines the HCl-accepting capabilities of organotins, this factor is important. It should be noted that industrial stabilizers usually contain other additives than the primary stabilizer, therefore they will have still lower tin concentrations.

Under practical conditions, the index of refraction permits us to differentiate between carboxylate-type organotins and sulfur-containing stabilizers, but only in the case of pure compounds.

All organotins absorb below cut off of sun spectrum (below 290 nm). There is a considerable difference in absorption of UV between various groups of tin stabilizers. Laurates have absorption maximum at 230 nm. All mercaptoacetic acid derivatives have only one peak at 238 nm for dimethyl- and dibutyl-tins but it is shifted to 225 nm in the case of diisooctyl organotin. Maleates have a single absorption maximum at around 238 nm. In contrast, UV spectrophotometric data offer useful information on mercaptopropionates and thioalkylates of dialkyltins. Mercaptopropionates, including dibutyltin β-mercaptopropionate and dibutyltin bis(iso-octyl mercaptopropionate), have their absorption maxima at 250 nm. Dibutyltin bis-thiododecane has two absorption maxima, at 230 and 250 nm.

IR spectra, as can be predicted from the chemical groups present, do not differ drastically, as basically the same bonds are available in all stabilizers since the Sn-S bond has practically no value in identification. The only clear difference is in the case of dibutyltin bis-thiododecane and dibutyl tin β-mercaptopropionate, as they have no absorption in the range from 2800 to 1500 cm^{-1}. These compounds can, therefore, easily be recognized from their IR spectrum. In other cases, the most useful means of detection is comparison of absorption intensity between various peaks. This means using the full spectra for comparison, as every group has a sufficient number of distinctive features, which can assist in identification. IR spectra alone definitely cannot form the sole basis for identification of organotin compounds, especially commercial products.

11.3.4.1 Properties and applications of commercial stabilizers

Table 11.15. Properties and applications of organotin stabilizers

Manufacturers: Galata Chemicals, Stannica LLC, PMC, Baerlocher, Akcros	
Commercial names: Mark 292, 292S, 645, 694, 1038, 1367, 1900, 1900S, 1915, 1921E, 1923, 1924, 1925, 1930, 1939F, 1940, 1941, 1971, 1974, 1982, 1984 E, 1987, 1989, 1993, 1998, 2100A, 2202, 2211, 2225, 2244, 2255, 2270F, 2284A, 2288, 2289, 2294, 2330, 2400, 2903, 2908, 2909, 2910, 2911, 2912, 2919, 2920, 3062, 3101, 3112S, 3160, 3173; Stannica DBTO, TTBT, TTOT; Thermolite 31, 108, 140, 161, 176, 190, 387, 890, 890F, 892WF; Advastab TM-181FS, TM-182, TM-283SP, TM-286, TM-404ER, TM-590, TM-599A, TM-691, TM-694, TM-697, TM-698, TM-3412; Baerostab M 25, M 25 S, M 25-85, M 26 SF, M 71, M170, X-AB-7, OM 62 A, OM 36, OM 69 S, OM 700, OM 710 N, OM 1000, OM 1400, DBTL/C, M 15, M 63, M 64; Akcrostab T-94CS, T-876, T-878, T-878M, T-5003B, T-5003R, T-5313, T-5314, T-5315, T-5316, T-5322, T-5507A, T-7020, T-7021; Tinstab BL-277; Interstab T-5201, T-5277, T-5278B, T-5311	
Chemical names: butyltin carboxylate, butyltin mercaptide, mercaptide/carboxylate, butyltin thioglycollate, methyltin mercaptide, methyltin reverse ester, octyltin mercaptide, butyltin maleate, octyltin maleate, butyltin dilaureate	
CAS#: 6683-19-8, 201687-58-3	**EC#**: 229-722-6, 200-464-6

Table 11.15. Properties and applications of organotin stabilizers

Mol. weight: 337-1117	**Melting**, °C: -40 to 27	**Decomp**, °C: 172 to >250	**Flash point,** °C: 99-280
Ref. index: 1.47-1.53	**Density**, 20°C: 0.89-1.19	**Viscosity**, mPas: 22-546	**Vapor pres**., Pa: n/a
State: most liquid	**Color**: clear to amber	**Color (Gardner)**: 1-9	**Odor**: low to mercaptan
Water solubility, %: insoluble		**LD50, rat**, mg/kg: 243-4440	
ACGIH, mg/m^3: 0.1		**OSHA**, mg/m^3: 2	
Biodegradation: 7 to 23 after 28 days		**Fresh water fish**: 96-h, mg/l: 0.6 to more than 1000	
Daphnia magna: 48-h, mg/l: 0.38 to 49		**Algae**, 72-h, mg/l: 1.4 to 260	
Composition: primary stabilizer: 40 to 96%; tin: 13.4 to 25%, sulfur: 0 to 18.7%, some contain butyl tin chlorides (1-3%); some grades phenol-free			
Exceptional properties: excellent light stability, excellent initial color, long-term color holding, prevents plateout, low odor, transparent, clarity, gloss, colorless, regrind stability, excellent cost/performance ratio, good whiteness, high shear application, chemical resistance, low extractability, low water absorption, easy printable and weldable, low fogging, kicker			
PVC processing methods: coating, extrusion, calendering, plastisol processing, blow molding, injection molding, foaming, blown film			
Product applications: roofing, pipe & fittings, profiles, packaging materials which comply with food regulations, conduit & duct, siding, window & door, film, fencing, bottles, sheets, deck, rail, automotive interiors, corrugated sheets for roofing, credit cards, coated fabrics			
Recommended addition rates, phr: 0.35 to 2			

11.3.4.2 Mechanisms of action

By comparison with metal soaps, the mechanism of organotin stabilizers is more complicated because tin is a four-valent metal, compared to usually two valent metals in metal soaps. Tin stabilizers have three types of bonds with metal: Sn–C, Sn–O, and Sn–S, compared with only M-O in metal soaps.

Before discussing chemical aspects that determine the possible participation of various bonds available in a molecule during chemical reactions, we might wish to look into another important factor, the physical component of reactivity. The physical state of a stabilizer under reaction conditions is practically not taken into account for metal carboxylates. Here, some investigators have pointed out the importance of the physical barrier of reaction.

Wirth[166] observed that alkyl length might affect the processability of stabilizer. Gupta[61] gave details of the conditions of sample preparation; e.g., dispersion of the stabilizer in PVC resin, concluding that the degree of dispersibility was determined by physical properties of the stabilizer and, in turn, affected the stabilizing efficiency of the composition. Szabo,[232] discussing the properties of dibutyltin bis(isooctyl thioglycollate), pointed out that it is an efficient stabilizer because of its compatibility with polymer. Brecker[211] stressed the importance of dialkyltin bis(isooctyl mercaptoacetate) because of the so-called resin plasticizing effect manifested by lower melt viscosity and the need to adjust lubrication when the stabilizer is changed. Safronov *et al*.[233] published results of physical studies of compatibility of PVC and tin stabilizers. Compatibility of PVC with liquid alkyltin alkylthioglycolate stabilizers was studied by isothermal calorimetry of mixing, DSC, DMA, and dielectric relaxation. The enthalpy of mixing of PVC was measured over the entire concentration range at ambient conditions.[233] It was found that all tested compounds

are compatible with PVC in a broad concentration range.[233] Tin stabilizers were found to form homogeneous mixtures with PVC. The excellent compatibility of tin stabilizers with PVC can be even visually observed from mixtures containing up to 90% stabilizers which had no boundaries in the cast films and were completely transparent in the temperature range of 270 to 400K.[233]

The saturation concentration of stabilizers is much higher than concentrations normally used in PVC stabilization. The compatibility of carboxylates decreases with the increase of the chain length of the alkyl, methyl derivatives being the most compatible. Strong interaction between the tin atom and PVC molecules is the underlining factor of compatibility.

Glass transition temperature shift caused by the presence of tin stabilizers is low (about 2°C), which suggests that tin carboxylates are efficient external lubricants.[238]

Glass transition temperature measurements also indicate that tin stabilizers show characteristics typical of antiplasticizers. The antiplasticizing effect contributes to the increase of the tensile strength and rigidity of PVC materials.[233]

Regarding the chemical reactions of stabilizers, it is important to know which groups connected to tin react first and what is the nature of the reaction products. To answer the last question, many researchers have devoted their studies to determining how far the proposition of Frye and Horst[36,38,234-236] might be confirmed in the case of organotin stabilizers. Both authors contended (see details in Section 11.2.1) that the thermal stability of PVC should increase if the labile centers of dehydrochlorination are replaced by another group that remains in the polymer chain.

This excellent compatibility also improves chemical reaction conditions. When a chlorine atom of the PVC chain associated with tin is allylic it is rapidly substituted by the thioglycollate group, which is one of important principles of stabilization.[233]

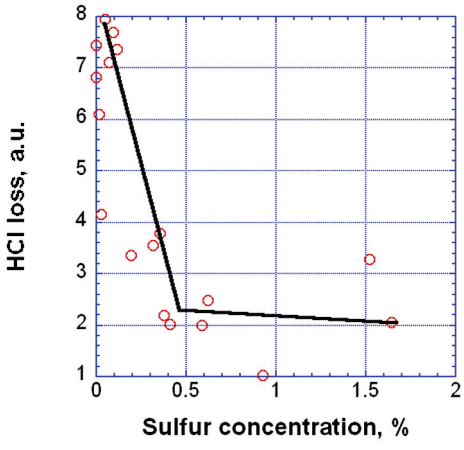
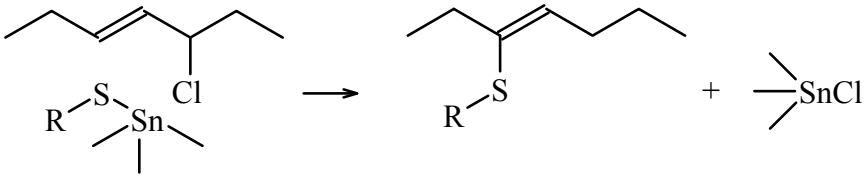


Figure 11.22. PVC dehydrochlorination rate versus sulfur content. [Data from Starnes, W. H.; Plitz, I. M., *Macromolecules*, **9**, 633, 1976.]

Starnes[212] pretreated PVC with $Bu_2Sn(SC_{12}H_{25})_2$ or its mixture with Bu_2SnCl_2, using much higher than usual quantities of these compounds in order to eliminate labile chlorines if possible. The resultant chlorine in the polymer was considerably decreased to the level of 51.8%. Figure 11.22 shows the PVC degradation rate as a function of the sulfur concentration in polymer. Positive changes evidently occurred in the polymer samples since the degradation rate of polymer was decreased, but it has yet to be proven that the reaction proceeds with the labile chlorine instead of modifying the whole polymer by statistical replacement. Studies with model compounds have revealed that allylic chlorines

react faster with an organotin stabilizers (including thioglycollates and maleates)[237] than with random chlorines.[6] The model compound of the head-to-tail PVC chain did not react with organotin stabilizers at PVC processing temperatures.[14,33] From this data, Ayrey[206] concluded that the reactivity of stabilizers with allylic chlorine determines their effectiveness in PVC stabilization.

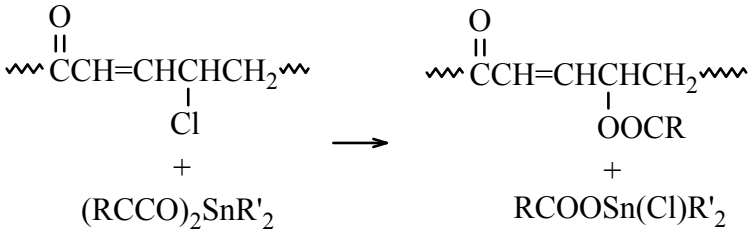
Frye[38,234-236] proposed the following reaction to illustrate chloroallyl substitution:



It was also observed that at low temperatures (393K), when the thermal rate of dehydrochlorination is almost negligible, the amount of reacted stabilizer was much lower than that expected from the concentration of chloroallyl groups.[206] It was simply demonstrated[166] that PVC thermal discoloration can be reversed by treatment with dibutyltin bis(isooctyl thioglycollate), which suggests that stabilizer reacts with chlorines in the vicinity of conjugated double bonds. The lower the molecular weight of the polymer (more unsaturations and labile chlorines at chain ends), the more the stabilizer reacted.[10] Taking into consideration these observations and those made by Starnes,[212] there is little doubt about the ability of organotin stabilizers to replace labile chlorine, especially when adjacent to a double bond. The question still remains open whether this reaction does not go too far, that is, whether chlorine in regular units of the chain is not replaced.

Comparing the two types of stabilizers, those containing sulfur and those sulfur-free, Coorey[209] discovered that dibutyltin maleate is unable to react with an isolated double bond, but it can reduce thermal degradation. Coorey's results are given in Figure 11.23.

Minsker[208] proposed the following reaction for tin carboxylates:



which resembles the substitution of carboxylic acid residue in place of labile chlorine, which is part of the mechanism of action of Cd and Zn carboxylates.

The other important factor for stabilization with organotins is their reactivity towards HCl and chlorine. In an alcoholic solution, dibutyltin dilaurate reacts with HCl much faster than do metal soap stabilizers.[10] There are no data on the reactivity of organotins in PVC formulations. For a model compound, the reactivity of organotins was very high.[14,33] It was also found that stabilizer conversion was independent of its concentration.[166] The

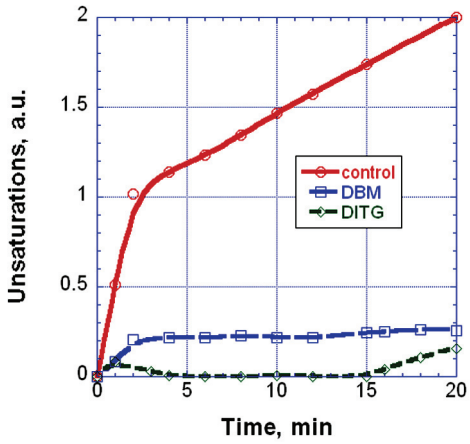


Figure 11.23. The effect of organotins on the formation of unsaturations during processing at 443K. DBM – dibutyltin maleate, DITG – dioctyltin bis(isooctyl thioglycollate). [Data from Cooray, B. B.; Scott, G., *Dev. Polym. Stab.*, **2**, 53, 1980.]

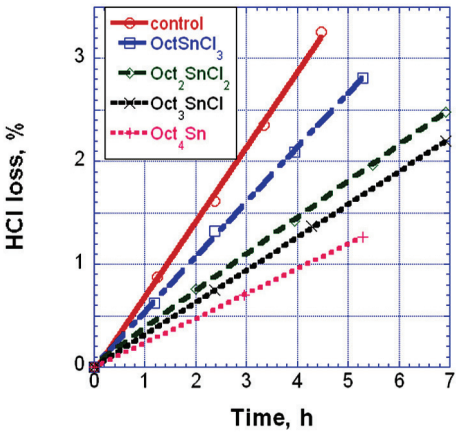


Figure 11.24. The effect of octyltin chlorides on the PVC dehydrochlorination rate at 448K. [Data from Wirth, H. O.; Andreas, H., *Pure Appl. Chem.*, **49**, 627, 1977.]

dehydrochlorination rate of PVC containing variable concentrations of stabilizer remained steady if the concentration of the stabilizer was above 0.5%, and the dehydrochlorination rate was decreased when the stabilizer concentration was below that level.[207] All these findings point to very high reactivity of organotins with HCl.

Wirth[166] studied the effect of octyltin chlorides on the dehydrochlorination rate of PVC (Figure 11.24).

The inclusion of tetra-alkyl tin produces a retarding effect on dehydrochlorination reaction similar to the partially reacted products with HCl. None of these compounds exhibits an induction period, which is an essential criterion for inclusion in the group of stabilizers.

The next question arises as to how many chlorine atoms can be bound by one molecule of tin stabilizer. Van Hoang,[17] investigating reactions of tin stabilizers with a model compound resembling allylic chlorine, found that the following reactions occur:

$$(C_6H_5)_2SnCl_2 + HCl \longrightarrow C_6H_5 + C_6H_5SnCl_3$$

$$C_6H_5SnCl_3 + HCl \longrightarrow C_6H_5 + SnCl_4$$

But several other researchers found that, even when there is an excess of HCl, R_2SnCl_2 is the only main product of reaction with model compounds.[14-16,212] Rockett[16] has demonstrated in detailed studies that formation of the reaction products of $RSnCl_3$ and $SnCl_4$ from R_2SnY_2 stabilizer is an exception and it occurs only when Sn–C bonds are

cleaved because of the presence of, for instance, phenyl rings. Therefore, we can write the reaction of industrially important stabilizers as follows:

$$RSnY_3 + 3HCl \longrightarrow RSnCl_3 + 3HY$$
$$R_2SnY_2 + 2HCl \longrightarrow R_2SnCl_2 + 2HCl$$

During thermal degradation process at least four reaction products can be present: R_2SnYCl, $RSnYCl_2$, R_2SnCl_2, $RSnCl_3$. The question immediately arises whether it is possible that these partially reacted products can exchange chlorine between themselves and with unreacted stabilizer. Burley and Hutton[29,30] answered this question and showed that the following reactions (and similar combinations) might take place:

$$R_2SnCl_2 + R_2SnY_2 \longrightarrow 2R_2Sn(Cl)Y$$
$$2RSnCl_3 + 3R_2SnY_2 \longrightarrow 2RSnY_3 + 3R_2SnCl_2$$
$$RSnY_2Cl + R_2SnY_2 \longrightarrow RSnY_3 + R_2SnYCl$$

This implies that products of stabilizer reaction tend to balance their chlorines, and even when monoalkyl stabilizer is used, $RSnCl_3$ is likely to appear at the end of the process.

It is important to evaluate how these chlorine-containing intermediates affect the thermal stability of PVC. Figure 11.24 above shows the retarding effect of dehydrochlorination by all three chlorine-containing components. Van Hoang[17] presented the results of his studies shown in Figure 11.25. These data were obtained from degradation of a model compound, and they are similar to those obtained by Wirth[166] for PVC with one essential difference. The difference is that in van Hoang's studies[17] $RSnCl_3$ accelerates the degradation of the model compound, whereas Wirth found that it has a retarding effect. It is very important to understand how the retardation effect occurs. From data quoted above it is clear that R_2SnCl_2 does not undergo any further chemical change, thus arousing interest as to how this compound may act. Wirth[18] explained this phenomena by isomerization or transfer of double bonds (reaction shown above), which might introduce rest Y into the chain. The isomerization may proceed according to the following scheme:

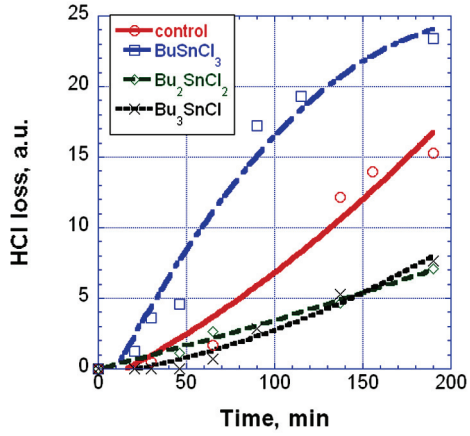
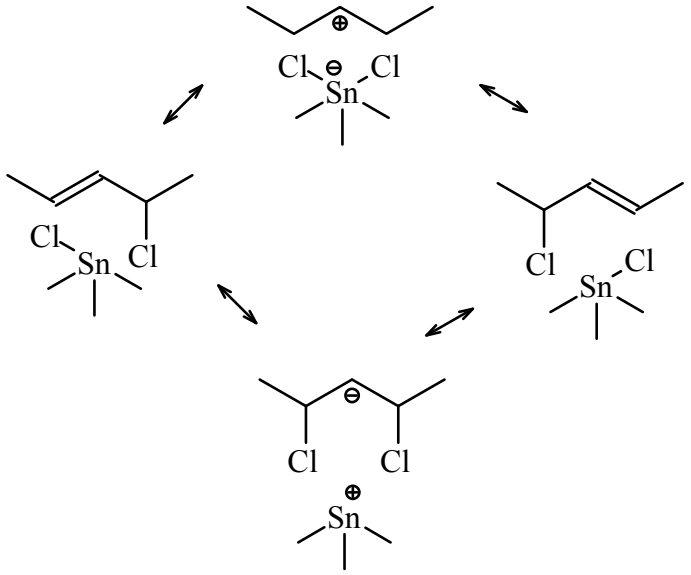
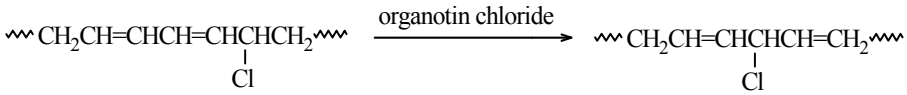


Figure 11.25. The effect of butyltin chlorides on the PVC dehydrochlorination rate at 453K. [Data from van Hoang, T.; Michel, A.; Guyot, A., *Polym. Deg. Stab.*, **4**, 213, 1982.]

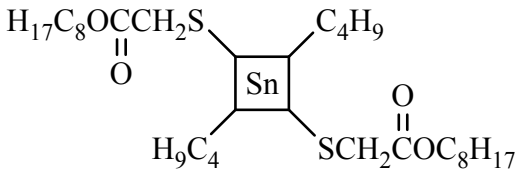


For polyene chain growth, this reaction could be written as follows:



Wirth's suggestion[18] is substantiated by well documented, experimental results for l-chlorobutene-2. It seems probable that observations for PVC will confirm these findings.

Internal coordination of the structure of organotin stabilizers is thought to be the other important factor for determining stabilizer performance.[211] Brecker,[211] comparing dibutyltin bis(dodecyl mercaptide) with dibutyltin bis(isooctyl mercaptoacetate), concluded that the latter is internally coordinated according to the following structure:



According to this concept, there is no restrained configuration, which, in turn, results in better steric hindrance to coordinate labile chlorine atoms in PVC as compared with dibutyltin bis(dodecyl mercaptide). Other authors have not commented on the structure of stabilizers until much later studies. Fisch *et al*.[239] conducted studies of PVC degradation by recording color changes of samples versus time of heating using color computer. Figure 11.26 shows an example of their data. If there was no stabilizer, there was no induction

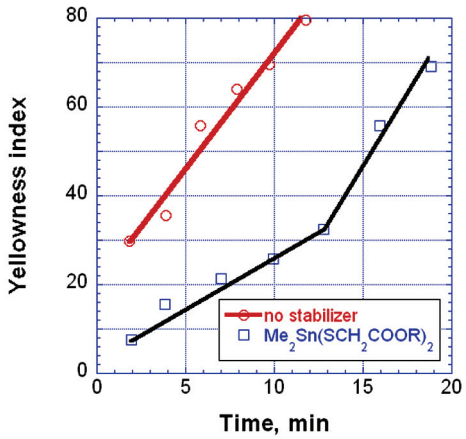
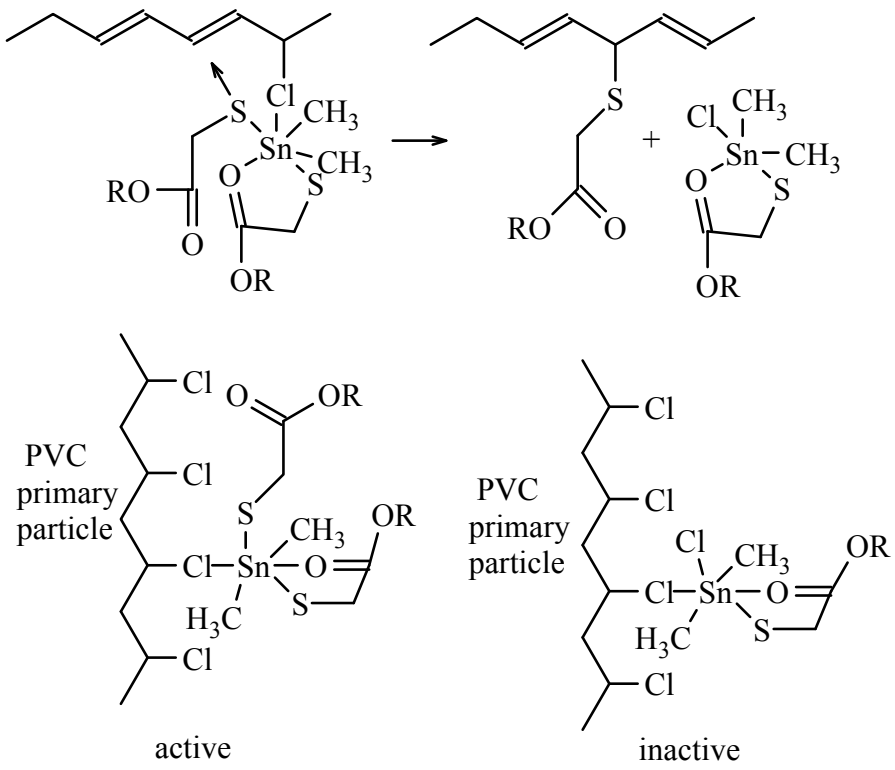


Figure 11.26. Yellowness index vs. time of heating for formulation with and without dimethyltin bis(2-ethylhexyl thioglycollate). [Data from Fisch, M. H.; Bacaloglu, R.; Biesiada, K.; Brecker, L. R., *J. Vinyl Additive Technol.*, **5**, 1, 45-51, 1999.]

period and linear increase in yellowness index was observed. The relationship of color change for stabilized PVC composition was also linear but had two different rates: one similar to the unstabilized composition and it was occurring after stabilizer was exhausted (after induction period) and the other before stabilizer was exhausted (before induction period) which was considerably lower. These two different rates characterize initial color and degradation rate. Studies of different stabilizing compounds by the same method (color evaluation) have shown that only $RSnY_3$, $RSn(Cl)Y_2$, and R_2SnY_2 give initial period. All other partially reacted stabilizers ($(RSn(Cl)_2Y$ and $R_2Sn(Cl)Y$) did not give induction period (meaning they did not stabilize color).[239] This seems to suggest that the last thioglycollate group from an alkyltin thioglycollate is not active in the stabilization of color. That is in agreement with the known fact that trialkyltin thioglycollates are not effective as stabilizers for PVC.[239] It was also observed that polymeric thioglycollates with one or two thioglycollate groups are not active in PVC stabilization, presumably because of the lack of conformational mobility that hinders the association of these groups with PVC chlorine atoms.[239] Now the question arises why it is so, since from the previous data we could see that all partially reacted stabilizers are able to react with HCl. Fisch *et al*.[238] postulated that alkyltin thioglycollates are associated with PVC molecules at the surface of its primary particles by weak coordination bonds between tin and chlorine atoms.[239] Tin is hexacoordinate in these complexes as it forms a stronger coordination bond with the carbonyl oxygen of one of the thioglycollate groups.[239] These thioglycollate groups cannot consequently be in intimate contact with the PVC molecules and thus they do not participate in the stabilization process.[239] But a second thioglycollate group on tin may replace the allylic chlorine by an allylic rearrangement according to the following scheme:[239]



The scheme shows why the last thioglycollate group of alkyl tin thioglycollates is not active as it forms a complex with tin and therefore it is not in contact with the PVC chlorine atoms.[239] Alkyltin tris(alkyl thioglycollates) are more effective PVC stabilizers than dialkyltin bis(alkyl thioglycollates) because they have two reactive groups in their molecules. Because of the method used (color measurements), the results of this study do not contradict previous results, which suggest that all Y groups are able to react with HCl.

Degradation studies conducted in solution suggest that substitution is only possible in the presence of HCl.[35,240,241] Substitution was found to proceed in the case of sulfur-free and sulfur-containing stabilizers.

From the discussion of chlorine-containing, partially-reacted stabilizers, it is evident that the number of alkyl groups bound to tin plays an important role in the stabilizer's efficiency. The efficiency of stabilizers was previously thought to follow the order: R_2SnY_2 > $RSnY_3$ > R_3SnY >> R_4Sn. As we know it today, only di- and tri-alkyltins are used as stabilizers and the best performance is expected from a mixture of the two.[242-245]

Compounds of type SnY_4 provide no stability and even contribute to a fast blackening, which is attributed to strong Lewis acidity. The stronger the Lewis acidity of the stabilizer, the more pronounced is its effect on PVC dehydrochlorination. Also, crosslinking is

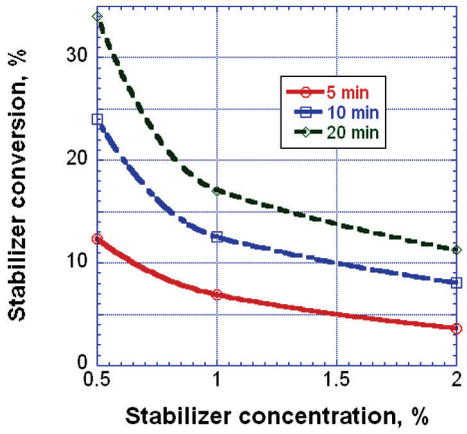


Figure 11.27. Dioctyltin bis(isooctyl thioglycollate) consumption versus its concentration in milling test at 453K vs. time. [Data from Wirth, H. O.; Andreas, H., *Pure Appl. Chem*., **49**, 627, 1977.]

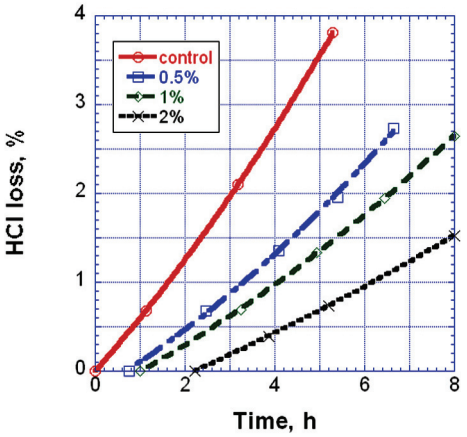


Figure 11.28. PVC thermal dehydrochlorination in the presence of varying amounts of dioctyltin bis(isooctyl thioglycollate) at 448K. [Data from Wirth, H. O.; Andreas, H., *Pure Appl. Chem*., **49**, 627, 1977.]

more evident with an increase in Lewis acidity, as demonstrated by Brecker,[211] who used a Brabender plastograph to determine stability of formulations containing different organotins. Lewis acidity can also explain the influence of alkyl (denoted by R) on the dehydrochlorination rate. Mossbauer's isomeric shift was used as a measure of Lewis acidity (the higher the value of the isomeric shift, the lower the acidity). Acidity increases with the length of alkyl chain decreasing (methyltin derivatives are more acidic than butyl and octyl). With acidity increasing, dehydrochlorination rate increases.[17]

The length of the alkyl chain also affects compatibility with PVC. The compatibility of dialkyltins decreases with an increase in the length of alkyl because of the more pronounced solvating properties of the part denoted by Y. The overall performance of organotin stabilizers can be demonstrated by data from Wirth's paper[166] (Figures 11.27 and 11.28).

The consumption of stabilizer is lower when its concentration in formulation increases. The induction period increases almost linearly with the addition of the stabilizer; whereas the higher the addition of stabilizer, the lower the dehydrochlorination rate. As demonstrated by Wirth[166] and Cooray,[209] there are several reasons why stabilizers are added. Wirth[166] assigned them two main functions:

- preventive functions: antioxidant effect, HCl binding, exchange of labile chlorine atoms, and complex formation,
- curative functions: addition of rests to the polymer chain.

Most of these functions have already been discussed, and only an antioxidant effect is left for further consideration. The rate of PVC dehydrochlorination in oxygen was decreased when dibutyltin bis(butyl thioglycollate) or dibutyltin bis(cyclohexyl maleate)

had been added,[213] which was explained by peroxide decomposition. Wirth[166] suggested that organotins could act as antioxidants according to the following scheme:

$$R_2Sn[S(CH_2)_nCOOR']_2 + HOOR'' \longrightarrow R_2SnO + HOR'' + \boxed{R'OOC(CH_2)_nS}_2$$

Armstrong[246] described this process as being performed in two stages. In the first stage, stoichiometric oxidation of sulfide was observed, and in the second, catalytic destruction of hydroperoxides occurred. This course of reaction was confirmed with model compounds.[246] Garrigues *et al*.[240] conducted studies of various formulations containing dioctyltin thioglycollate in air and under an argon blanket. Induction period in the presence of air is 2-3 times shorter than at inert conditions, which shows that presence of organotin does not give sufficient protection against oxidation and usually other means are required to protect polymer against radical oxidation.

Summarizing results of the above investigations, one may enumerate the following features of organotins' action:

- HCl-binding capacity: both groups of stabilizers (sulfur-free and sulfur-containing) show good reactivity towards HCl. In the process of HCl binding, chlorine-containing derivatives are formed that retard the dehydrochlorination rate.
- Allylic chlorine could be replaced by sulfur-containing organotins and probably by sulfur-free tin stabilizers.
- Sulfur-containing stabilizers take part in the isomerization of double bonds, because of which polyene sequences might be shortened and terminated. This reaction is not specific for sulfur-free stabilizers.
- Sulfur-containing organotins may react with isolated double bonds, whereas others cannot.
- Tin maleates may react with double bonds because of the Diels-Alder reaction scheme.
- Sulfur-free stabilizers may substitute chlorine by carboxylic acid rest in a manner similar to the one proposed for metal soap stabilizers.
- Partially-reacted stabilizers may react between themselves in order to balance their chlorines.
- All organotins may take part in color retardation as a result of the formation of complexes and the isomerization of double bonds acting through their chlorides.
- Sulfur-containing stabilizers are capable of decomposing peroxides, and maleates may also exhibit some retarding effects.

11.3.4.3 Costabilizers

Costabilizers, very important for other groups of stabilizers, are much less applicable in the case of tin stabilizers. Garrigues *et al*.[240] studied several costabilizers with dioctyltin thioglycollate, such as epoxidized soybean oil, β-diketone derivatives, and dihydropyridine derivatives. None of studied costabilizers gave substantial improvement of stabilizing performance. This is mostly due to the fact that, unlike $ZnCl_2$, products of reaction of tin stabilizers with HCl have some stabilizing qualities and if they increase dehydrochlorination rate they do not have strong catalytic influence.

Epoxy compounds are sometimes added together with tin stabilizers. It is expected that they may reduce influence of HCl as well as transport chlorine between various reaction products of tin stabilizers with HCl which may help to balance their chlorines and thus reduce Lewis acidity strength which affects dehydrochlorination rate.[58]

Similar to divalent metal carboxylates and hydrotalcite-like acid absorbers or scavengers, tins stabilizers are combined with acid absorbers. These are zeolite type costabilizer particles of submicron size coated with tin stabilizers.[248]

Costabilization in the case of tin stabilizers is rather related to the use of various combinations of different tin compounds to obtain an advantage in either total efficiency, balance between initial color and long-term stability, or balanced production efficiency and outdoor protection. This type of costabilization makes mixtures of monoalkyl and dialkyl tin derivatives the most popular among tin stabilizers.

Organotin stabilizers may contain mixtures of different tin compounds but also mixtures with other metals.[249-251] One invention reveals an organotin stabilizer which contains aluminum and divalent metals such as zinc and/or magnesium.[249] This combination gives good initial color, long-term stability and low water absorption.[249] Another composition comprises a complex mixture of alkyl tin carboxylates and/or mercaptides, and of monoalkyltin sulfides and dialkyltin sulfides which perform very well on outdoor exposure.[250] A composition of dioctyltin mercaptide with zinc stearate of phosphite ester was used as an effective stabilizer.[251] These and many other examples show that tin stabilizers can also be effectively improved by development of synergistic mixtures.

11.3.4.4 Other findings

Most companies produce stabilizers that were rightly called in one Ciba-Geigy (presently BASF) invention by the name "Eintopf," which in German means soup serving as the first and the second course in one. The extent of this type of policy can be as broad as that of some stabilizers, which include every additive needed for processing that can be associated with stabilization or lubrication, and they are meant for narrow application; for instance, for one extruder type. Also, some stabilizers are based on one chemical type of organotin but include small quantities of other stabilizing components, which, due to synergistic effect, enhance the performance of the main stabilizer.

Tin stabilizers can be seen as all-purpose stabilizers, but because of their higher price they are mainly used in processing rigid PVC, in which the higher cost of stabilization is rewarded with high efficiency of equipment use and higher processing rates. Tin stabilizers are mainly employed in production of sheets, profiles, general-purpose and potable water pipes, sidings, films, foils, and bottles. Tin stabilizers are commonly used in extrusion, calendering, blow molding, and injection molding, but also in plastisol processing. From the point of view of final product properties and use, one may distinguish between general thermal stabilization, stabilization for outdoor use, production of articles in contact with food products, production of foamed materials, and processing of compositions, including fluorescent pigments.

Tin maleates and carboxylates are suggested for use when weather resistance is important. As their thermal stabilization efficiency is lower, these stabilizers are usually not used alone, but in composition with thioglycollates and a UV absorber.

Articles meant for food packaging or production employ two groups of organotins, e.g., dioctyltin bis(isooctyl thioglycollate) and estertins, because of their lower toxicity (more details in Chapter 12). If outdoor stability is demanded, they are mixed with dioctyltin maleate polymeric stabilizer.

Low water blush haze and low extractability was obtained by a combination of a Lewis acid compound, tin stabilizers and epoxy compound.[252] Combination of zinc and tin stabilizers gives stable liquid stabilizers.[253] Various other solvents, such alcohols and phenols are added in order to prevent tin stabilizers from precipitation.[254]

Poly(dioctyltin maleate-styrene-methyl acrylate) was synthesized by radical solution polymerization.[255] It has better stabilizing efficiency than poly(dibutyltin maleate-styrene-methyl acrylate) and dibutyltin maleate (DBTM).[255] It also has better compatibility with polymer in PVC processing.[255]

Alkyltin sulfanyl diester thiols that have from one to three terminal thiol groups are suitable for thermal stabilization of PVC, compositions.[256] The dimethyltin bis[di(2-mercaptoethyl)succinate] stabilizer and its blend with the monomethyltin derivative exhibit superior long-term heat stability in comparison to the mixture of monomethyltin tris-(2-ethylhexylthioglycollate) and dimethyltin bis-(2-ethylhexylthioglycollate) – commonly considered as one of the most efficient stabilizers.[256]

Some organotins are very efficient kickers. In rigid profiles wherein high efficiency of the foaming system is important, which is a limiting factor in extrusion rate and product quality, tin-containing kickers are commonly used. Argus (presently Galata Chemicals) also offered a tin stabilizer developed for compositions containing fluorescent pigments, which was based on dibutyltin bis(iso-octyl maleate).

Dialkyltin bis(alkyl thioglycollates) have always been the most common tin stabilizers. In the past they were used in the form of either butyl or octyl derivatives, but now they are more frequently used in the form of methyl derivatives, especially in the USA. This is attributable to the cheaper production of dimethyltin dichloride. Recently interest has grown in the application of mono- and di-alkyl (mainly methyl) thioglycollates in which monoalkyl derivative amounts to 5%-40%. These very efficient thermal stabilizers can be used in small quantities. So-called estertins are products having, as their most interesting feature, the lowest toxicity among tin stabilizers.

The dosage of organotin stabilizer varies, depending on the raw materials used, the technology of processing, the type of machinery (multi-screw extruders need about three times less stabilizer as compared with single-screw machinery), the composition of stabilizer, and the application of the final product. Single-component or older types of stabilizers are usually used in doses of 1-3 phr, whereas the most advanced products are added in quantities as small as 0.25 to 0.4 phr.

Most tin stabilizers are liquids, but some contain dissolved solid materials that sometimes show a tendency to crystallize from solution.

UV absorption of industrial tin stabilizers is far from the range of sunrays; these substances cannot, therefore, be directly involved in photolytic reactions. Also, degradation temperatures of the stabilizers are sufficiently high to guarantee thermal stability while stabilizing the polymer.

11.3.5 ORGANIC STABILIZERS

11.3.5.1 Epoxidized compounds

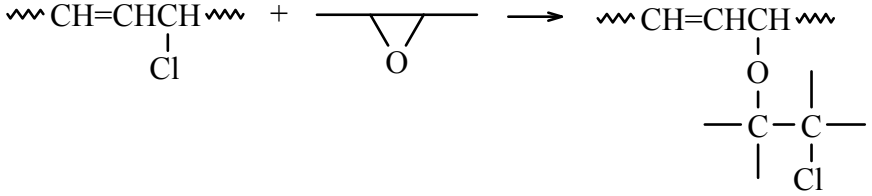
11.3.5.1.1 Properties and applications of commercial stabilizers

Table 11.16. Properties and applications of epoxidized stabilizers

Manufacturers: Akcros, Arkema			
Commercial names: Lankroflex E2307, ED6, L; Vikoflex 4050, 5075, 7170, 7190			
Chemical names: epoxidized linseed oil, epoxidized soybean oil, epoxidized tallate ester, epoxidized octyl stearate, epoxidized propylene glycol dioleate			
Mol. weight: 1000	**Melting**, °C: -10-0	**Boiling**, °C: n/a	**Flash point,** °C: 260-290
Ref. index: 1.45-1.48	**Density**, 25°C: 0.92-1.03	**Viscosity**, mPas: 30-660	**Oxirane**, %: 4.4-9
State: liquid	**Color**: clear, yellowish	**Color (Gardner)**: 1-4	**Odor**: fatty
Water solubility, %: 0.01-0.03		**Solubility in solvents**: butanol, esters, ketones (misc)	
Exceptional properties: high oxirane concentration, non-toxic, improves weathering, improves long-term stability, lubricating properties, secondary plasticizer, resistance to water extraction			
PVC processing methods: calendering, coating, dip coating, extrusion, injection molding, rotational molding, slush molding			
Product applications: Ca/Zn stabilized materials, organotins, rigid and plasticized PVC, plastisols, organosols, bottles for mineral water, rework, flooring, roofing, coated fabrics, wallcoverings, films, sheet, medical applications, automotive interiors and moldings, intravenous tubing, pipe, cap liners, seals, blood bags, food wrap film, meat trays, upholstery			
Recommended addition rates, phr: 1 to 5			

11.3.5.1.2 Mechanisms of action

Michel and coworkers[10,17,257] studied the possible mechanisms of action of epoxy compounds using low-molecular models of PVC. Anderson and McKenzie's[258] proposed the following reaction mechanism:



Anderson's studies,[258] conducted on model compounds, showed that the above reaction was catalyzed by cadmium chloride. Later, Michel[259] found it to be applicable to zinc chloride as well. He demonstrated that other side reactions might occur, such as cationic oligomerization of the oxirane ring, complexing of zinc chloride, and hydrolysis of the ether bond when excessive amounts of HCl are formed.[260]

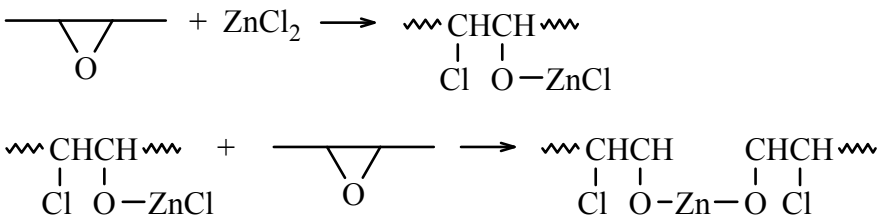
The mechanism of action of epoxy compounds, in the presence of the organotins' reaction products, was also explained. In the first stage, the complexed epoxy compound was thought to be polarized; the chlorine atom was then attacked, and the epoxy carbocation was formed, which was again attacked by the polarized oxygen.[17] Finally, the α-chloro-ether was formed, and a tin atom was coordinated by another epoxy molecule.

From the data on model compounds, one may see that the epoxidized compounds were thought to perform the following functions:

- react with labile chlorine atoms, at least those in the neighborhood of double bonds,
- bind HCl,
- complex zinc chloride and cadmium chloride,

just to mention the most important ones.

Complexing of $ZnCl_2$ was also later proposed by Iida *et al*.[261,262] based on studies of PVC compositions. The proposed mechanism is described by the following equations:



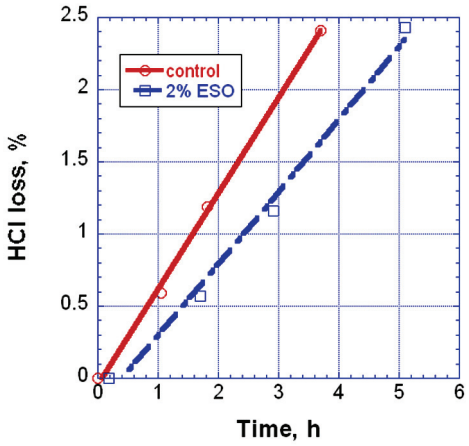


Figure 11.29. The rate of PVC dehydrochlorination at 448K with and without epoxidized soybean oil. [Data from Wirth, H. O.; Andreas, H., *Pure Appl. Chem*., **49**, 627, 1977.]

Although publications[261,262] contain numerous data which stress improvement of PVC stability, the mechanism proposed is of a speculative nature.

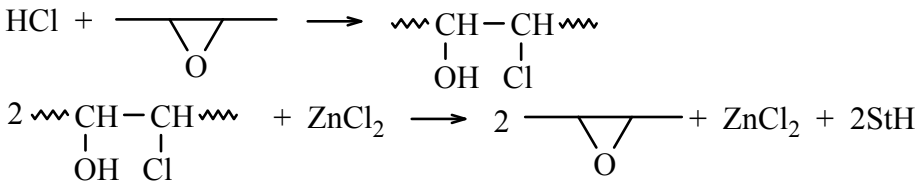
Based on the above results it can be concluded that epoxy compounds act in a similar way to that expected from a primary stabilizer, but they cannot be used alone to maintain PVC stability, as Figure 11.29 shows. Wirth[19] compared the rate of dehydrochlorination of PVC including epoxy compound to that of polymer without any additive.

It is evident that the induction period practically does not exist; however, there is a slight decrease in the dehydrochlorination rate. The latter fact can be explained by Minsker's work;[174] he found that epichlorohydrin does not catalyze PVC dehydrochlorination, and he also confirmed that neither epoxy compounds nor their reaction products affect the formation of double bonds. Both conclusions agree with visual observations which show that, when epoxy compounds are incorporated alone, the sample is degraded the same way as it would have been without additives present. At the same time, these facts alone do not contradict the results obtained by Michel and his team, as he concluded that a metal chloride is needed as a catalyst.

Gilbert and Startin[20] used the best available techniques at the time of their research, such as liquid scintillation counting, steric exclusion chromatography, and GC-MS, to demonstrate the inapplicability of results obtained with model compounds. They detected a small amount of the epoxy group bound to PVC but only in the range of the usual concentrations found in samples which were not treated thermally at all. Only after blackening of the sample was the concentration of the epoxy group bound to the chain slightly increased, which was contrary to Michel's suggestion. Commenting on Anderson's paper, Gilbert and Startin said:[20] "The attraction of model systems to facilitate isolation and identification of reaction products is easy to understand, but the results presented here make it evident that data so obtained cannot be correlated with the true situation in stabilized polymer system."

These investigators[20] also discovered that epichlorohydrin is present in a thermally degraded sample only at a very low level, and its concentration is not affected by the presence of calcium/zinc stabilizer.

Wypych[21] found that a solution of HCl and an epoxy compound retains high electric conductivity, most likely because of unreacted HCl. After the addition of zinc stearate, the electrical conductivity of the solution was decreased when about 60% of zinc stearate had reacted. Addition of more zinc stearate liberated epoxy compound, which was later fully recovered. This led to the following mechanism confirmed by chromatographic data:[21]



These reactions suggest that epoxy compounds take part in HCl transfer from polymer to stabilizer. It is known[12] that incorporation of an epoxy stabilizer with the zinc stearate more than doubles the induction period; therefore, the reaction mechanism must be different from that in which zinc stearate alone is used. The difference can be explained by either Michel's[10,257] or Anderson's works:[258] Zinc chloride is either bound by epoxy compound, or "the transfer mechanism" plays an essential role. There is no sufficient data to decide between the two solutions.

If metal soap is present in the mixture, one may predict that reactions go through a set of parallel, competitive acts including:

- substitution of acid residue from metal carboxylate, substitution of epoxy compound through either the mechanism proposed by Ida[263] or Anderson,[258]
- hydrolysis of ether bonds,
- HCl transfer,
- metal chloride binding by epoxy compounds.

It is possible that future research will yield important studies on PVC that will allow us to find a further details of the mechanism of action of epoxy compounds in mixtures

with other stabilizing components. So far, after almost a quarter of century, "the transfer mechanism"[21] is commonly accepted.

11.3.5.1.3 Research findings

Benaniba *et al*.[264,265] conducted research on the properties of epoxidized sunflower oil in stabilization of PVC. Figure 11.15 contains data which show the effect of epoxy stabilizer on the effectiveness of Ca/Zn stabilizers. Figure 11.30 shows that epoxidized sunflower oil is slightly more effective than the commonly used epoxidized soybean oil.[264] The authors concluded that the stabilizing effect of epoxidized oils cannot be observed by using them without the synergetic metal soaps and that the synergism between epoxidized stabilizers and metal soaps results from the reduction of the initial rate of dehydrochlorination due to the reaction between HCl evolved and epoxy stabilizer and metal soaps which reduces its catalytic effect on the degradation of PVC.[264]

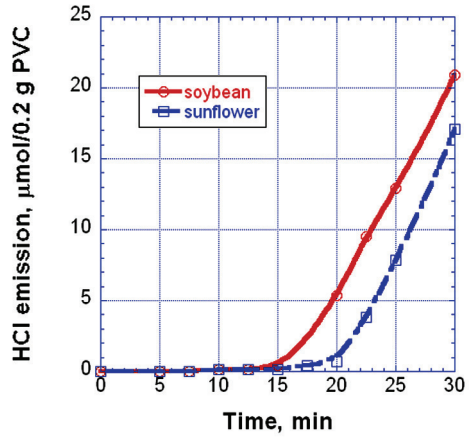


Figure 11.30. HCl emission from PVC sheet with Ca/Zn stabilizer and either epoxidized soybean or sunflower oil at 170°C. [Data from Benaniba, M. T.; Belhaneche-Bensemra, N.; Gelbard, G., *Polym. Deg. Stab*., **74**, 3, 501-505, 2001.]

Braun *et al*.[93] synthesized methacrylate-based copolymers with 2,3-epoxypropyl methacrylate and investigated them as costabilizers for PVC. It was found that these polymers are capable of improving PVC stabilization. The costabilizing effect depends on the amount of functional groups. The costabilizers interact with most kinds of commercial PVC stabilizers.[93]

Rubber seed oil was epoxidized to be used as PVC costabilizer.[266,267] In addition, metal soaps were synthesized from epoxidized acids of rubber seed oil. The derivatives had good stabilizing effect.[266,267]

A stabilizing composition containing Ca/Zn stabilizer and epoxidized glyceride were patented as a stabilizing system for PVC molding compounds.[268] Also, compositions and methods of plasticization of PVC with plasticizers containing epoxidized fatty acid esters has been patented.[269] Effective system containing zinc stabilizers, epoxidized soybean oil, and phosphites have been patented for use in stabilization of phosphorescent PVC films.[270]

Epoxidized soybean oil improved fusion of plastisols stabilized with $ZnSt_2$.[271] Higher tensile strengths of epoxy stabilizer containing plates indicated more complete gelation of the plastisols.[271]

Epoxidized soybean oil undergoes thermal degradation in the presence and absence of PVC to form ring-opened products.[272] In the absence of PVC, the degradation reaction is intermolecular formation of ether. The degradation in the presence of PVC is facilitated by reaction with hydrogen chloride generated by polymer degradation.[272] Fully epoxi-

dized soybean oil (7.0 wt.% oxirane oxygen) contains two types of oxirane groups: type I which begins to undergo thermal ring-opening at about 175°C and type II which opens at > 325°C.[272] Both ring openings are exothermic and irreversible.[272] The type I oxirane groups account for approximately one-third of the total oxirane content of fully epoxidized soybean oil whereas the partially epoxidized soybean oil (3.28 wt.% oxirane oxygen) contains only type II oxirane rings.[272]

A method of analysis of composition of epoxidized oils has been developed based on gas chromatography to facilitate efforts in controlling migration of additives into food and from medical instruments into body fluids.[273] γ-irradiation of medical devices shows that the 15-20 phr epoxidized soybean is an optimum concentration for radiation-stable products.[274] It should be noted that according to European Farmacopea for PVC tubes only up to 10% of epoxidized soybean oil or epoxidized linseed oil can be used.[275]

The formation of a crosslinked network by a polymerization reaction of the epoxy groups in the epoxidized soybean oil occurs in plastisol type PVC but not in suspension PVC.[276] The ring opening of the epoxy which starts the polymerization of epoxidized soybean oil is likely catalyzed by an additive used in the polymerization of plastisol PVC.[276] Fatty acid epoxy esters are used as bio-based plasticizers/stabilizers.[277] In addition to sustainability, composition containing epoxidized linseed oil was found to be biodegradable (68% in 6 months).[278] It was also confirmed that epoxidized soybean oil can be used of efficient plasticizer in food packaging material.[279]

A blend containing one or more fatty acid esters and one or more bio-based oils was epoxidized to form the epoxidized composition.[280] This process has several advantages over a process of forming a blend of already epoxidized fatty acid esters and epoxidized bio-based oils.[280] The epoxidation of a blend containing soy methyl ester and vegetable oil has the following advantage: the soy methyl ester acts as a solvent for epoxidation of the vegetable oil, thus eliminating normally used organic solvent, such as, toluene.[280] This simplifies the process and reduces cost of production.[280]

11.3.5.2 Phosphites

11.3.5.2.1 Properties and applications of commercial stabilizers

Table 11.17. Properties and applications of phosphite stabilizers

Manufacturers: Galata Chemicals, SI Group, Dover, Akcros			
Commercial names: Mark CH 55, CH 66, CH 300, CH 301, CH 302, CH 304, CH 305, TNPP; Weston 437, 439, DHOP, DPDP, DPP, DPTDP, EHDP, PDDP, PNPG, PTP, TDP, THOP, TLP, TPP; Ethaphox 326, 327, 368; Doverphos 4, 4-HR, 6, 7, 8, 9, 10, 11, 12, 49, 53, 72, 213, 253, 613, 675, HiPure 4; Akcrostab CH-300, CH-301; Interstab CH-55			
Chemical names: trinonylphenyl phosphite, phenyl diisodecyl phosphite, diphenyl alkyl phosphite, tris(2,4-di-t-butylphenyl) phosphite, distearyl pentaerythritol diphosphite, bis(2,4-dicumylphenyl) pentaerythritol diphosphite and many more			
CAS#: 3806-34-6, 26741-53-7, 26523-78-4, 31570-04-4, 154862-43-8		**EC#**: 223-276-6, 247-952-5, 247-759-6, 250-709-6	
Mol. weight: 310-839	**Ref. index**: 1.45-1.56	**Density**, 20°C: 0.85-1.18	**Flash point,** °C: 130-218
Viscosity, mPas: 15-8600	**State**: liquid, flakes, powder		**Odor**: odorless - mild
Thermogravimetric analysis: from 1% 250°C; 8% 300°C; 20% 325°C; 42% 350°C to 1% 225°C; 4% 300°C; 8% 350°C			
Color: clear to yellowish	**Color (Gardner)**: 2-3	**log K_{ow}**: 4.64	
ACGIH, mg/m^3: 3 (solid)	**OSHA**, mg/m^3: 15 (solid)	**LD50, rat**, mg/kg: 1,600-19,500	
Water solubility, %: <0.01		**Fresh water fish**: 96-h, mg/l: 49-100	
Daphnia magna: 48-h, mg/l: 0.42-510		**Algae**, 72-h, mg/l: 75.2-100	
Composition: phosphorus: 4.2 to 13.3%			
Exceptional properties: hydrolysis stable, excellent initial color, provides long-term stability, FDA approved, improves gas fading performance, reduced plate out			
PVC processing methods: calendering, coating, extrusion, blow molding, injection molding			
Product applications: flooring, wall covering, roofing, pond and pool liners, film, upholstery, apparel, hose, tubing, wire, artificial leather			
Recommended addition rates, phr: 1 to 3			

11.3.5.2.2 Mechanisms of action

Organic phosphites are believed to perform the following functions:[19,281-297]

- HCl binding,
- substitution of labile chlorine,
- addition to double bonds,
- metal chloride binding,
- decomposition of peroxides,
- improvement of transparency.

If one compares these functions with, let's say, the action of tin stabilizers, it may be assumed that phosphites act in a similar fashion; the true effect is different.

Figure 11.31 shows that aliphatic phosphite increases dehydrochlorination rate and aromatic phosphites partially decrease the dehydrochlorination rate. None of the phosphites shows a substantial induction period which is a typical characteristic of stabilizer. Figure 11.32 shows that aryl phosphite practically does not react with HCl, whereas aliphatics

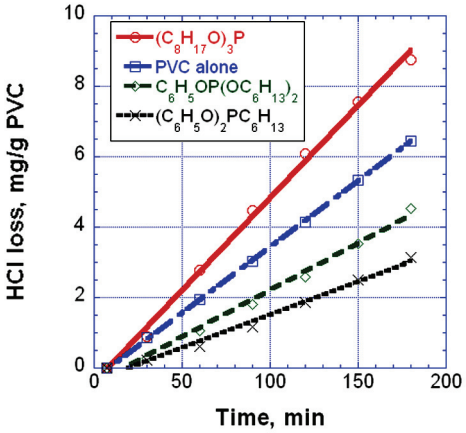


Figure 11.31. PVC dehydrochlorination rate in presence of various phosphites. [Data from Pobedimskii, D. G.; Mukmeneva, N. A.; Kirpitchnikov, P. A., *Dev. Polym. Stab.*, **2**, 125, 1980.]

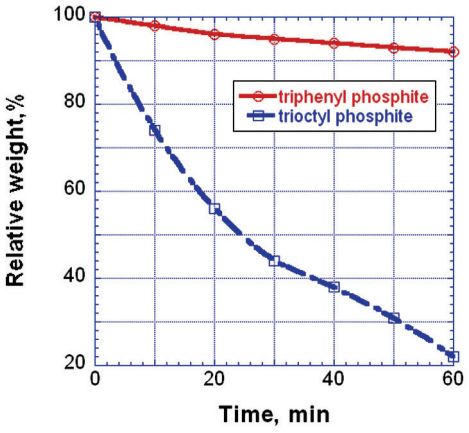


Figure 11.32. Relative weight loss during reaction of phosphites with anhydrous HCl at 180°C. [Data from Jakupca, M. R.; Harr, M. E.; Stevenson, D. R., *J. Vinyl Additive Technol.*, **10**, 2, 99-103, 2004.]

phosphite gradually reacts with three molecules of HCl, which can be written in the form of the following equations:[23,24,283]

$$(RO)_3P + HCl \longrightarrow (RO)_2PHO + RCl$$

$$(RO)_2POH + HCl \longrightarrow ROP(OH)HO + RCl$$

$$ROP(OH)HO + HCl \longrightarrow H_3PO_4 + RCl$$

Each consecutive reaction produces increasingly stronger acid with the strongest phosphoric acid produced in the last reaction. Figure 4.71 shows the effect of pK_a of different acid on PVC thermal stability. The stronger the acid, the lower the pK_a constant and the lower the stability of PVC (the higher the thermostability number A, the more stable the formulation; for full explanation on thermostability number A, see references 298,299).

The data explains the results included in Figure 11.31. Only alkyl phosphite is able to produce phosphoric acid according to Figure 11.32. Phosphoric acid is the strongest acid (the lower pK_a) and therefore it increases dehydrochlorination rate. The other two acids formed have substantially higher pK_a constants and therefore their influence on dehydrochlorination rate is smaller than their effect on decrease of dehydrochlorination rate resulting from efficient binding of HCl which is not able to catalyze dehydrochlorination.[283,297]

The reactivity of phosphites towards HCl is considered to be lower than that of metal soaps,[285] which explains why phosphites exhibit a short induction period.

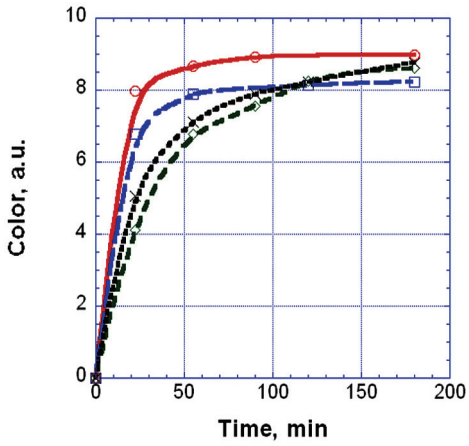


Figure 11.33. PVC color change in presence of various phosphites. Labels are the same as in Figure 11.33. [Data from Pobedimskii, D. G.; Mukmeneva, N. A.; Kirpitchnikov, P. A., *Dev. Polym. Stab.*, **2**, 125, 1980.]

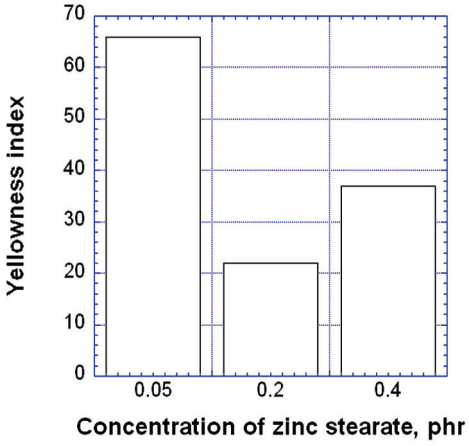


Figure 11.34. Yellowness index of formulation containing different concentrations of zinc stearate. (PVC 100, DOP 45, $CaCO_3$ 20, epoxidized soybean oil 5, stearic acid 0.25, diphenyl ethylhexyl phosphite 2 parts, zinc stearate - variable). [Data from Stevenson, D. R.; Harr, M. E.; Jakupca, M. R., *J. Vinyl Additive Technol.*, **8**, 1, 61-69, 2002.]

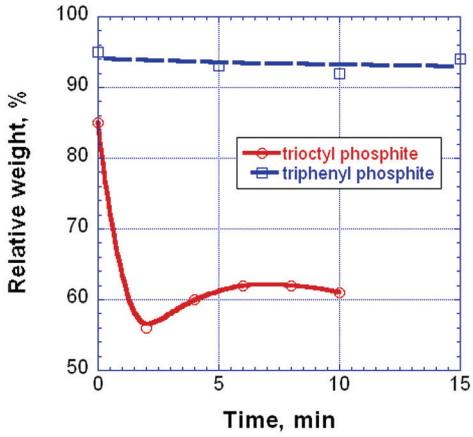


Figure 11.35. Reaction of phosphites with 5 wt% $ZnCl_2$ at 180ºC. {Data fro Jakupca, M. R.; Harr, M. E.; Stevenson, D. R., *J. Vinyl Additive Technol.*, **10**, 2, 99-103, 2004.]

Color changes from the beginning when phosphites are used alone (Figure 11.33). The comparative influence of three phosphites on color changes follows the same pattern as their influence on dehydrochlorination (Figure 11.31) and it also can be explained by the differences in the strength of acids formed in the process of reaction with HCl. Addition of stabilizer, such as, for example, zinc stearate, preserves initial color for a period of time which depends on the amount of primary stabilizer in a complex way. Figure 11.34 implies that there is a concentration at which zinc stearate is the most effective. This concentration depends on the entire formulation because it has to balance initial color and long-term stability. Essential to the mechanism of action of phosphite is its ability to react with $ZnCl_2$.[8,23,56] Figure 11.35 shows that aliphatic phosphite rapidly reacts with $ZnCl_2$ but aryl phosphite does not.[56]

The following reaction scheme has been previously proposed:[8]

$$ZnCl_2 + 2P(OR)_3 \longrightarrow (RO)_2P\underset{\underset{O}{\|}}{Zn}\underset{\underset{O}{\|}}{P}(OR)_2 + 2RCl$$

It is agreed that phosphites are also able to replace labile chlorine atoms and thus affect the dehydrochlorination rate,[23,24,56,286-288,295] but disagreement existed concerning the type of group containing labile chlorine atoms that is able to react with phosphite. Russian authors[23,283,284,288] proposed, based on reactions with model compounds, that the model chloroallylic group cannot react with phosphites, and only the ketochloroallyl group undergoes this reaction. This supposition was not generally accepted (similar to influences of the ketochloroallyl group on initiation of dehydrochlorination) and it is commonly agreed now that the following reaction takes place:[19,24,56,286,287,295,296]

$$(RO)_3P + \sim\!CH{=}CH\underset{\underset{Cl}{|}}{CH}\!\sim \longrightarrow \sim\!CH{=}CH\underset{\underset{O=P(OR)_2}{|}}{CH}\!\sim + RCl$$

This reaction was seen to be not very selective because up to 5% phosphorus was found in PVC after intensive dehydrochlorination.[259,289] No further comments on this matter can be found in the existing literature. Guyot[24] has indicated that the substitution reaction is catalyzed by zinc chloride and that the phosphorus-containing group can be hydrolyzed during the more advanced stages of polymer degradation; this is similar to the mechanism attributed to fatty acid residues. If this statement is correct it does not agree with the observation that 5% phosphorus remain after long dehydrochlorination. In model compounds, Guyot also found that aryl phosphites are not able to substitute into the polymer chain and do not react with labile chlorine atoms.[24]

Phosphites are considered to be able to react with hydroperoxides according to the following equation:

$$R'OOH + P(OR)_3 \longrightarrow R'OH + O{=}P(OR)_3$$

Therefore, it is possible that they may take part in the termination step of oxidation reactions, which is important in prevention of thermooxidative and photolytic degradation.

Jakupca *et al*.[56] provided experimental evidence that phosphites are oxidized when exposed to heat and air in a model system (paraffin dispersion). It is noticeable that both types (aryl and allyl) of phosphites are active in reaction with hydroperoxides but alkyl phosphite are substantially more reactive (Figure 11.36).

This function of phosphites makes them important costabilizers because metal soaps, unlike organotins, do not exhibit these capabilities. Reaction with hydroperoxides is especially essential for the weathering characteristics of PVC formulations.

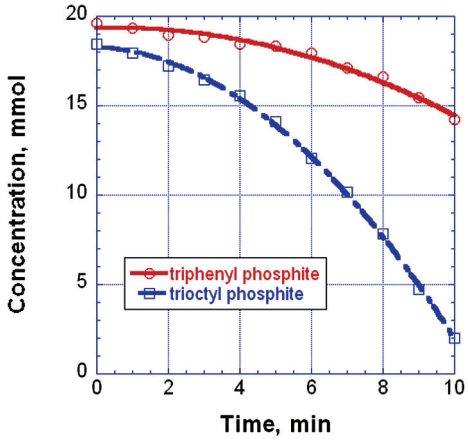


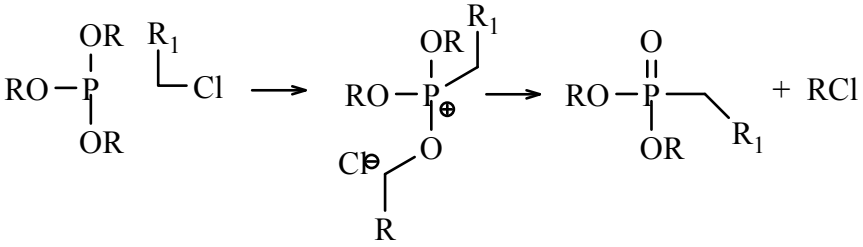
Figure 11.36. Concentration of phosphite exposed to air at 180°C (20 mmol phosphite in paraffin). [Data from Jakupca, M. R.; Harr, M. E.; Stevenson, D. R., *J. Vinyl Additive Technol.*, **10**, 2, 99-103, 2004.]

11.3.5.2.3 Costabilizers

Phosphites by themselves are costabilizers. Jacupca *et al.*[56] show that phosphites can also benefit from costabilization with epoxidized soybean oil (Figure 11.37). $ZnSt_2$ with TOP in the formulation (a) gives very good stability and color retention. When $ZnSt_2$ is consumed, $ZnCl_2$ is formed, contributing to the rapid decomposition of PVC. If TOP is used as the sole stabilizer (b), rapid darkening occurs later but the early color is slightly yellow, which indicates that TOP is not effective as a primary stabilizer. If ESO and TOP are used together (c), darkening is further delayed, but the early color is still inferior. ESO apparently reacts with HCl and reduces its catalytic effect on PVC degradation. If all three stabilizers were used together (d), they form a synergistic mixture giving the best early color and long-term stability. TPP gives inferior early and midterm color.

11.3.5.2.4 Research findings

The so-called Michaelis-Arbuzov reaction is frequently quoted in literature regarding phosphites.[56,295,296] The reaction was first described in 1898.[300-302] It outlines transitional steps of reaction of phosphite with either HCl or $ZnCl_2$ to obtain phosphonate and alkyl chloride:



Internal rearrangement from transitional state to final products usually requires heat and in many cases also catalysis.

Using spin measurement (see polaron mechanism of PVC degradation) it was determined that the stabilization effect of alkyl phosphites improves with alkyl chain length increasing.[290]

Trinonylphenyl phosphite (considered non-toxic costabilizer) was used to stabilize PVC for medical applications.[293] It performed its functions during processing but did not affect stability of PVC during γ-sterilization.[293]

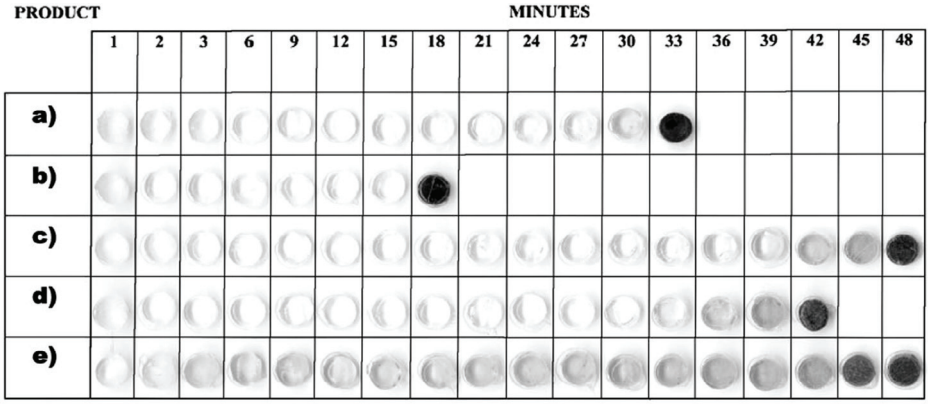


Figure 11.37. Thermal stability at 180°C. Brabender evaluation of PVC formulations: a) 3 phr TOP, 0.30 phr $ZnSt_2$, b) 3 phr trioctyl phosphite, TOP, c) 3 phr TOP, 3 phr epoxidized soybean oil, ESO, d) 3 phr TOP, 0.30 phr $ZnSt_2$, 3 phr ESO and e) 3 phr triphenyl phosphite, TPP, 0.30 phr $ZnSt_2$, 3 phr ESO. (base formulation: PVC 100, DOA 50, and stearic acid 0.2 parts). [Adapted, by permission, from Jakupca, M. R.; Harr, M. E.; Stevenson, D. R., *J. Vinyl Additive Technol.*, **10**, 2, 99-103, 2004.]

In restabilization of PVC wastes, a system of costabilizers has been proposed and it performed well.[294] The system contained phenolic antioxidant, phosphite, and HALS.[294]

Complex phosphite esters such as poly(dipropylene glycol) phosphites and alkyl bisphenol phosphites outperform simple phosphite esters as replacements in Ca/Zn stabilized systems.[295] These and other similar phosphites are proposed now for partial (only a very small amount of zinc carboxylate is needed for betterment of initial color) or complete replacement of heavy metal stabilizers.[296]

Liquid organic phosphites, based on pentaerythritol, were patented[303] for PVC stabilization. They are used in combination with Ba/Zn stabilizers to give phenol-free formulations.

PVC membranes for swimming pool liners were obtained by coating with PVC containing Ba/Zn carboxylate, alkyl phosphite, and benzophenone UV stabilizer.[304] An older invention[305] shows a combination of tin stabilizer with zinc carboxylate and phosphite – a direction which is exploited in order to reduce amount of tin stabilizers.

A composition comprising a mixture of two alkylaryl phosphites was patented. A mixture of two phosphites is a liquid at ambient conditions.[306] Phosphites were stabilized against hydrolysis by the use of amines.[307]

11.3.5.3 Phenolic antioxidants

11.3.5.3.1 Properties and applications of commercial stabilizers

Table 11.18. Properties and applications of phenolic antioxidants

Manufacturers: Clariant, Addivant, BASF, Si Group			
Commercial names: Hostanox O 3, O 310, OSP, SE 4; Lowinox CA22-50D, GP45; Anox 20, 70, 330, IC-14; Irganox 245, 245 FF, 245 DW, 1076, B 1171, Irgastab PVC 76; Ethanox 330, 330P, 376			
Chemical names: octadecyl 3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate, pentaerythritol tetrakis(3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate), benzenepropanoic acid, 3-(1,1-dimethyl)-4-hydroxy-5-methyl-1,2-ethanediyl bis(oxy-2,1-ethanediyl) ester, terakismethylene(3,5-di-t-butyl-4-hydroxydrocinnamate)methane, 1,1,3-tris(2'-methyl-4'-hydroxy-5'-t-butylphenyl)butane, phenol, 2,2'-ethylidenebis[4,6-bis91,1dimethylethyl)-, 1,3,5-trimethyl-2,4,6-tris (3,5-di-tert-butyl-4-hydroxybenzyl) benzene			
CAS#: 96-69-5, 1709-70-2, 1843-03-4, 2082-79-3, 6683-19-8, 27676-62-6, 35958-30-6, 36443-68-2, 41484-35-9		**EC#**: 202-525-2, 216-971-0, 217-420-7, 218-216-0, 229-722-6, 248-597-9, 252-816-3, 253-039-2, 255-392-8	
Mol. weight: 358-1178	**Melting**, ºC: 50-241	**Decomp.**, ºC: >220 to >350	**Flash point,** ºC: >150 to 289
Ref. index: n/a	**Density**, 20ºC: 0.94-1.14	**Viscosity**, mPas: 200-400	**Vapor pres**., kPa: 6.7
Thermogravimetric analysis: 10% at 278 to 365			
State: solid (a few liquid)	**Color**: white to yellow	**Color (Gardner)**: 2-8	**Odor**: odorless to slight
Water solubility, %: 0.01-0.001		**Solubility in solvents**: methanol, acetone, xylene	
ACGIH, mg/m^3: 3	**OSHA**, mg/m^3: 15	**LD50, rat**, mg/kg: >2000 to >10000	**log K_{ow}**: 8.24
Biodegradation: non-biodegradable to partially biodegradable		**Fresh water fish**: 96-h, mg/l: 0.14 to >100	
Daphnia magna: 48-h, mg/l: 0.16 to >1000		**Algae**, 72-h, mg/l: >30 to >1000	
Exceptional properties: good stability, high extraction resistance, low volatility, can be used with phosphites, FDA approved			
PVC processing methods: extrusion, injection molding			
Product applications: used as polymerization and process stabilizer; chain stopper in polymerization; appliance			
Recommended addition rates, %: 0.05 to 1			

11.3.5.3.2 Research findings

Use of phenolic antioxidants, in spite of a large number of commercial products available, is quite limited in PVC. The major use is polymerization, but also some formulations used in medical applications may contain antioxidants.[308-310] Studies of Irganox 1076 and 1011 show that 30-40% antioxidant becomes inactive when a dose of 10 kGy is applied; when the dose was increased to 50 kGy, the loss of antioxidant increased to 61-66%.[308] The increase in yellowness index was related to the polyene formation in PVC and quinone and hydroquinone formation from phenolic antioxidants due to radiation and thermal exposures.[309]

Oxidation of the PVC resin is believed to be a significant cause of compound darkening during exposure to γ-radiation.[310] Studies have shown that phenolic antioxidants worsen the problem, probably because of the aromatic groups in their structure.[310]

In addition to the effects of irradiation, the performance of phenolic antioxidants is controlled by their volatility and decomposition at process temperatures.[311]

In food contact and medical grade PVC, good stabilization was obtained by a combination of zinc carboxylate, alkyl ester of thiodipropionic acid, and phenolic antioxidant.[312]

A halogen containing polymer in the form of an aqueous suspension or emulsion contains a partially hindered phenolic antioxidant and selected sulfur containing antioxidants, which are both solid at 20°C.[313] This composition has increased thermal stability in the compounding stage.[313]

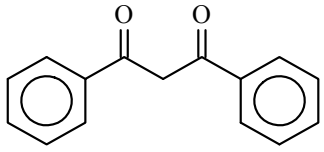
11.3.5.4 Multiketones

11.3.5.4.1 Properties and applications of commercial stabilizers

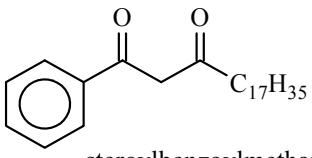
Table 11.19. Properties and applications of multiketone stabilizers

Chemical names: β-diketone, β-ketoester, dibenzoylmethane, stearoylbenzoylmethane, dehydroacetic acid, pyrrolidine-2,4-dione			
CAS#: 120-46-7, 58446-52-9, 520-45-6, 3777-89-7		**EC#**: 204-398-9, 261-257-9, 208-293-9	
Mol. weight: 168-386	**Melting**, °C: 56-111	**Boiling**, °C: 219-269	**State**: powder
Water solubility, %: <0.1		**Solubility in solvents**: methanol and other solvents	
Exceptional properties: binding metal chlorides			
PVC processing methods: various which use Ca/Zn and similar stabilizers			
Product applications: costabilizer, especially for zinc and magnesium containing stabilizers			
Recommended addition rates, phr: 0.2 to 1.5			

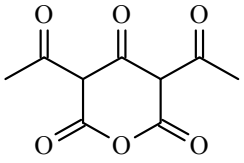
β-diketones are added to the formulations of stabilizers to enhance their properties. The individual compounds can also be purchased from speciality organic manufacturers (they were produced in past by Rhodia). Their formulas are given below:



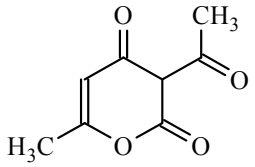
dibenzoylmethane



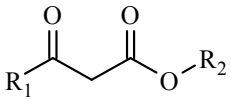
steroylbenzoylmethane



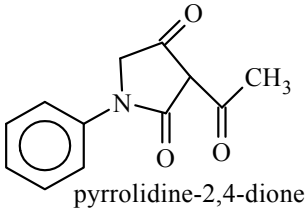
DATHP



dehydroacetic acid



β–ketoester



pyrrolidine-2,4-dione

11.3.5.4.2 Mechanisms of action

β-diketones are believed to replace allylic chlorines in the PVC backbone.[89] But the most important characteristic of β-diketones is their capability to form complexes with zinc salts. Spectroscopic evidence (infrared, fluorescence and phosphorescence) suggests that pyrrolidine-2,4-diones also form complexes with metallic salts.[89] The complexes of Zn carboxylates with pyrrolidine-2,4-diones dissociate more easily upon heating than the complexes with other diketones (see formulas above), which increases concentration of free stabilizer.[89,118,314] Easier thermal dissociation of these complexes results in more efficient replacement of active chlorines and, therefore, superior heat stabilizing properties.[89]

Guyot *et al*.[240,315-316] suggest that β-diketone compounds replace allyl chlorine by alkylation but only if metal soap stabilizer (e.g., Zn carboxylate) is present.

It has to be underlined that until now the above suggested mechanisms are speculative explanations of the reasons that these costabilizers improve performance of primary

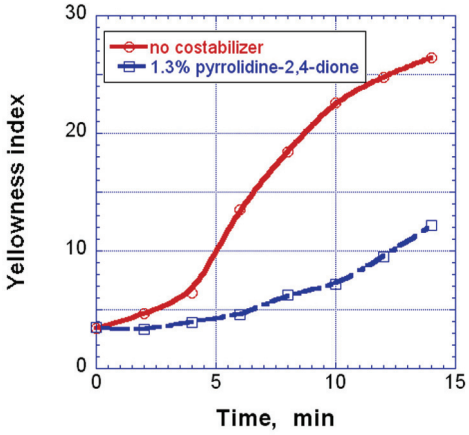


Figure 11.38. Yellowness index vs. time for PVC formulations containing Ba/Zn stabilizer with and without diketone costabilizer. [Data from Burley, J. W., *J. Vinyl Additive Technol.*, **3**, 3, 205-209, 1997.]

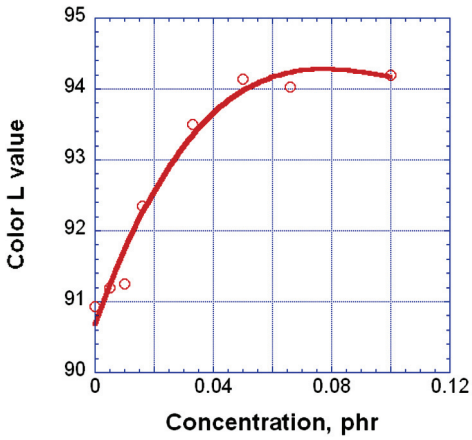


Figure 11.39. Effect of concentration of pyrrolidine-2,4-dione on color retention by extrudate containing Ca/Zn stabilizer. [Data from Burley, J. W., *J. Vinyl Additive Technol.*, **3**, 3, 205-209, 1997.]

stabilizers. Experimental data[290] show that diketones decrease spin number because of the effect of their resonant structures.

11.3.5.4.3 Costabilizers

A quaternary stabilizing system has been reported which contains calcium and zinc carboxylates, stearylbenzyl β-diketone, SMB, and 1,4-dihydropyridine diester, DHP.[316] Synergistic effect of DHP and SBM in air is believed to be a result of participation of costabilizers in reaction with oxygen, reaction with allylic chlorine, and binding $ZnCl_2$.

11.3.5.4.4 Other findings

Figure 11.38 shows that diketone costabilizer decreases color formation. Figure 11.39 shows that only small quantities of costabilizer are necessary to obtain substantial improvement in color retention.[89]

β-diketones were found to increase stability of medical PVC composition to γ-radiation exposure.[308] The stabilizing effect was enhanced when hydrotalcite was used as an acid scavenger.

Diketone costabilizers have been known for a long time. In 1978, Rhone-Poulenc Industries began their long list of inventions which included application of diketones and costabilizers.[317] A long list of β-diketones was included in their first patent and experimental examples showed substantial improvement of PVC stability.[317]

Zinc stannate and hydroxystannate were used as heat stabilizers together with β-diketones, 1,4-dihydropyridine or α-phenylindole.[318] Magnesium and zinc salts of benzoic and fatty aliphatic acids were used together with mannitol and β-diketone.[319] Two patents for manufacturing of diketones have also been filed.[320,321] Organotin stabilizers were also improved by the use of diketones.[240,322] More recently, many stabilizing combinations were developed because it became necessary to replace very efficient stabilizers such as

lead and Ba/Cd by non-toxic Ca/Zn carboxylates.[323] Here, inventions from the past became very handy because it was not possible to obtain good initial and long-term stability without β-diketones and/or other costabilizers. Around the end of the 20th century, β-diketones were suddenly called[89] "new costabilizers" and used to solve industry's problems.

Synergistic combination of metal stearates, β-diketones, and hydrotalcites was used in PVC stabilization.[324] β-Diketones substitutes allylic chlorides and inhibited formation of long polyene responsible for darkening.[324]

11.3.5.5 Other costabilizers

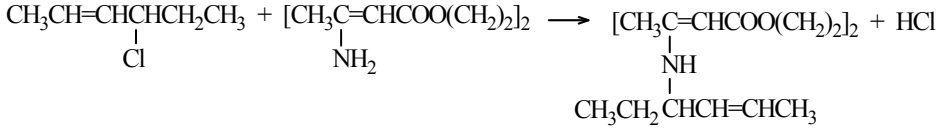
11.3.5.5.1 Properties and applications of commercial stabilizers

Table 11.20. Properties and applications of other costabilizers

Manufacturers: Galata Chemicals, PMC
Commercial names: Mark 6045, 6045 AMC, 6087 AMC, Stavinor D507
Chemical names: aminocrotonic acid ester, perchlorate (sodium perchlorate), α-phenylindole, dihydropyridine derivative, 6-amino-1,3-dimethyluracil, sodium tetraborate, sodium phenyl phosphinate
Composition: some perchlorates are adsorbed on the silica surface
Exceptional properties: reduces melt viscosity, resistance to staining with urethane foam
PVC processing methods: calendering, extrusion, injection molding
Product applications: rigid, semirigid, and plasticized PVC, automotive interior, film
Recommended addition rates, phr: 1 to 3

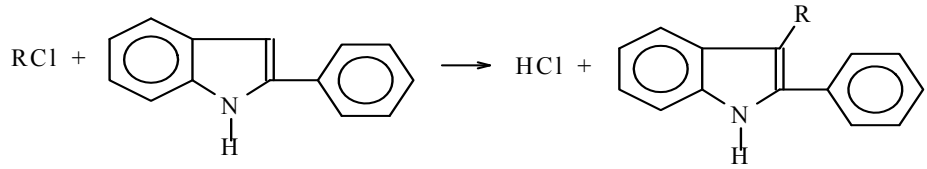
11.3.5.5.2 Mechanisms of action

β-aminocrotonic acid derivatives stabilize PVC, with the induction period depending on the concentration of stabilizer. The products of reaction increase the PVC dehydrochlorination rate (Figure 11.40). Michel and his coworkers[24,325,326] have presented the mechanism of action of β-aminocrotonic acid esters which can be explained by the following equation:



The equation, based on model studies, shows that the derivative of aminocrotonic acid is able to replace allylic chlorine, but does not show the reasons for the induction period. The same authors[24,324,325] postulated that butanediol-β-aminocrotonate may delay the formation of zinc chloride when it is used together with zinc stearate. Wirth[19] observed that β-aminocrotonic acid esters may perform better when they are used together with antioxidants, and that thermally discolored PVC may recover its color when treated with β-aminocrotonic acid ester.

α-phenylindole compounds retard initial discoloration and delay blackening.[257] The model studies show that phenylindole derivatives react with allylic chlorines according to the following equation:[257]



Michel and van Hoang[257] point out that the indole derivative cannot be hydrolyzed by HCl therefore the stabilizing effect is permanent.

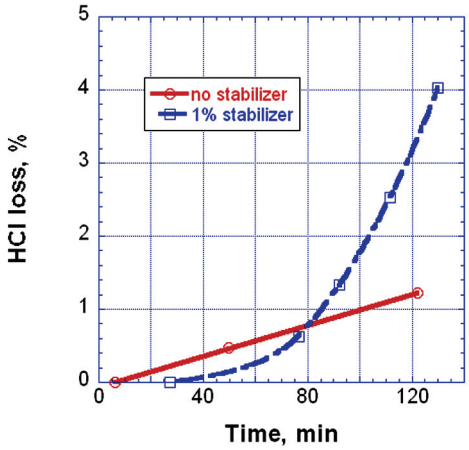
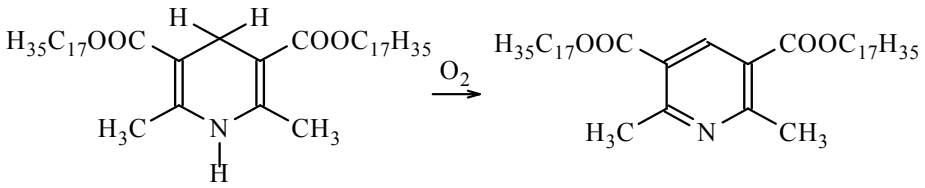


Figure 11.40. The effect of thiodiethylene glycol bis-β-aminocrotonic acid ester on the dehydrochlorination rate. [Data from Wirth, H. O.; Andreas, H., *Pure Appl. Chem*., **49**, 627, 1977.]

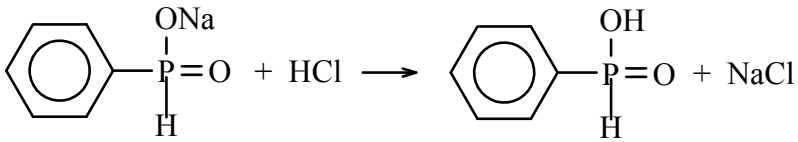
Pentaerythritol is an example of long-term costabilizer.[314] It has no influence on initial color formation but increases induction time.[314] For this reason it is sometimes selected as a costabilizer to perform this particular function.[327] It is more suitable for colored materials because it imparts some yellowness. Benavides *et al*.[327] suggest that pentaerythritol forms complexes with $ZnCl_2$, which delay dehydrochlorination by inhibition of the catalytic activity of $ZnCl_2$. An increased number of polyenes was observed in formulations containing pentaerythritol.[294] It is apparent from this summary of studies that the mechanism is speculative and requires further work.

Dihydropyridine derivatives (e.g., 2,6-dimethyl-3,5-dicarbododecyloxy-l,4-dihydropyridine) perform three major functions in PVC stabilizing formulations, according to Garrigues *et al*.[240] They act as hydrogen donor to polyene sequences by which they shorten long sequences and thus reduce absorption of visible light, coordinate the zinc atom by which they reduce the catalytic effect of $ZnCl_2$, and prevent oxidation according to the following scheme:[240]



In the presence of air the induction period is reduced because dihydropyridine derivative is oxidized and it cannot perform hydrogenation.[240] The oxidized dihydropyridine derivative acts only as a complexing agent for ZnCl[326] During the initial period, the absorption of visible light practically does not change.[240]

Sodium phenyl phosphinate, SPP, was found to react with HCl but did not affect color changes.[295] The following reaction occurs:[328]



6-amino-1,3-dimethyluracil and sodium tetraborate contributed to the increase of the induction period.[328] The advantage of adding sodium tetraborate into the formulation is

similar to that of hydrotalcites which can also scavenge HCl by reacting with the hydroxide groups. This reaction allows hydrotalcite-like clays to be used as HCl scavengers in PVC stabilization in an ion-exchange reaction.[328]

Thiol plasticizers/stabilizers have been reported[329] and patented.[330] Based on technological studies, which show oven stabilities and time to yellowing to be similar to formulation containing Ba/Zn and lead stabilizers, it is speculated that they act by reacting allylic chlorines and substituting into double bonds in the PVC chain, according to the following equations:[329]

$$RCl + R'SH \longrightarrow RSR' + HCl$$

$$\sim\!\sim(CH{=}CH)_n\underset{\displaystyle Cl}{\underset{|}{C}}H\sim\!\sim + R'SH \longrightarrow \sim\!\sim\underset{\displaystyle SR'}{\underset{|}{C}}H(CH{=}CH)_{n-1}\underset{\displaystyle Cl}{\underset{|}{C}}H_2CH\sim\!\sim$$

Aryl thiols are more reactive than aliphatic thiols towards allylic chlorines.[328]

11.3.5.5.3 Costabilizers

Costabilizers discussed in this section are used in many combinations[24,240,314,327,328] to take advantage of different functions which they are able to perform, as previously discussed.

11.3.5.5.4 Other findings

Sodium perchlorate, $NaClO_4$, was advantageously used in stabilization of PVC with various other costabilizers. The most useful stabilizers in combination with perchlorate were epoxy compounds and zeolite.[331] Stabilizer combination included perchlorate, hydrotalcite, and dihydropyridine.[332] Perchlorate was applied to the surface of hydrotalcite or zeolite.[299] Indole derivatives (or other nitrogen containing compounds such as carbamides or enamines) were used in combination with perchlorate salt.[333]

N,N-dimethyl-6-aminouracil was used in combination with zeolites and/or hydrotalcites to stabilize rigid or semi-rigid PVC.[334] Zinc carboxylate was used in stabilizing composition with zinc zeolite and hydrotalcite.[335]

N, N-dimethyl-6-amino-uracil, N-monomethyl-6-amino-uracil, and N-monomethyl-6-amino-thiouracil were synthesized *via* a precipitation method.[336] Stabilizers were able to replace labile chlorines in PVC and absorb HCl produced from PVC dehydrochlorination.[336] The initial color and long-term stability of PVC products were remarkably improved by synergistic mixture with zinc stearate.[336]

Basic zinc cyanurate was investigated as a thermal stabilizer for PVC.[337] PVC thermal stability is enhanced compared with zinc stearate. Further improvement is achieved by the addition of calcium stearate and epoxidized soybean oil.[337]

Composition for injection molding is stabilized by the mixture of Ca/Zn salt, hydrotalcite, β-diketone, and polyol.[338]

11.3.6 UV STABILIZERS

UV stabilizers discussed below are only given as a general example. Their mechanisms of action and applications are discussed in detail in a monographic source specially devoted to the subject (Handbook of UV Degradation and stabilization).[339] The types of UV stabilizers used in PVC and other polymers and their properties are discussed in detail in Databook of UV Stabilizers.[340]

11.3.6.1 Organic UV absorbers

11.3.6.1.1 Properties and applications of commercial stabilizers

Table 11.21. Properties and applications of organic UV absorbers

Manufacturers: Baerlocher, BASF, Addivant, Clariant, Cytec, Everlight, Ferro, Prospector, Kingsfield			
Commercial names: Baerostab B 200 P; Uvinul 3008, 3026, 3027, 3028, 3029, 3030, 3033 P, 3034, 3035, 3039, 3434 C; Lowilite 22, 27, 28, 55, 94; Hostavin 3041 DISP, 3206 LIQ, 3310 P, 3326 P, ARO 8 P, B-CAO, PR-25, PR-31 P, VSU P; Cyasorb UV-24, UV-531, UV-9, UV-2337, UV-5411 EF, UV-5411, UV-5365; Chimassorb 81; Eversorb 10, 11, 12, 13, 51, 52, 53, 71, 72, 73, 74, 75, 76, 77, 78, 79, 80, 81, 82, 89, 109, 234; UV-Chek AM300; Uvasorb HEB, S5; Uvanone 3C			
Chemical names: cyanoacrylate, benzophenone, benzotriazole, bis-benzoxazole, oxanilide			
CAS#: 131-53-3, 131-57-7, 1843-05-6, 2440-22-4, 3147-75-9, 3864-99-1, 3896-11-5, 5232-99-5, 6197-30-4, 7128-64-5, 23949-66-8, 25973-55-1, 70321-86-7, 82493-14-9, 125304-22-4		**EC#**: 205-026-8, 205-031-5, 217-421-2, 219-470-5, 223-383-8, 223-445-4, 226-029-0, 228-250-8, 230-426-4, 245-950-9, 247-384-8, 274-570-6, 279-979-3	
Mol. weight: 225-448	**Melting**, °C: -56 to 202	**Boiling**, °C: >400 to 477	**Flash point,** °C: 114 to 475
Ref. index: n/a	**Density**, 20°C: 1.00-1.38	**Viscosity**, mPas: 450-1050	**Vapor pres**., hPa: 0.1-4.6
Thermogravimetric analysis: from 1% at 143°C, 2% at 156°C, 10% at 188°C to 0.8% at 200°C, 6.4% at 250°C, 19.5 at 275°C to 5% at 295°C			
State: powder and liquid	**Color**: white to yellow	**Color (Gardner)**: 2-8	**Odor**: odorless
Water solubility, %: <0.00073 to <0.04		**Solubility in solvents**, %: acetone 2-105, chloroform 13-61, ethanol 0.1-4, toluene 0.05-50, DOP 2.5-20	
ACGIH, mg/m^3: 3	**OSHA**, mg/m^3: 15	**LD50, rat**, mg/kg: >2000 to >10,000	**log Kow**: 7.25
Biodegradation: 0% to <70% 28 days		**Fresh water fish**: 96-h, mg/l: 9 to >100	
Daphnia magna: 48-h, mg/l: 15 to 643		**Algae**, 72-h, mg/l: >100 to >100	
Exceptional properties: low volatility, good compatibility			
PVC processing methods: blow molding, coating, extrusion, calendering, injection molding			
Product applications: roofing, hoses, geomembranes, packaging, film, sheet, wire & cable, molded products, tents, tarpaulins, pool liners, flooring, automotive body side molding, instrument panels, glove boxes			
Recommended addition rates, phr: 0.025 to 2 (coatings 3-4 times more than plastics)			

11.3.6.1.2 Mechanisms of action

Phenyl salicylate is photochemically converted on irradiation to dihydroxybenzophenone according to the following reaction:

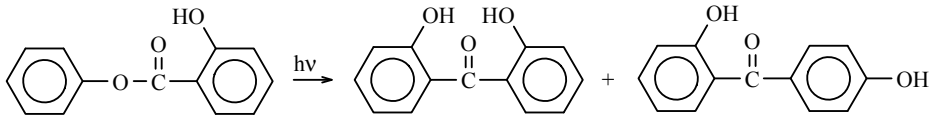
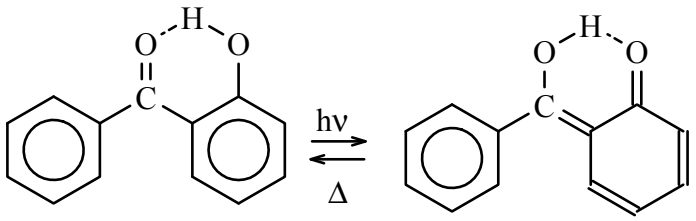


Photo-initiated Fries-rearrangement affects the physical properties of the stabilizer. The absorption maxima for the original compound, at about 240 and 310 nm, are shifted to the longer wavelength, which gives a better protection to the polymer, but, because the absorber itself is changing color, it causes the polymer mixture to yellow. Because photoconversion is not an immediate process, it is customary to use these stabilizers together with another additive, for instance a benzophenone derivative, to improve the initial protection to the material.[342] Salicylates are thought to be able to disperse energy in the form of fluorescence and to participate in the transfer of energy.[343]

2-hydroxybenzophenones offer an improvement over derivatives of salicylic acid because their normal structure resembles the product of the Fries-rearrangement of the salol. 2-hydroxybenzophenone has only one absorption maximum at about 340 nm. The introduction of a second auxochrome has a hypsochromic effect, and the second absorption maximum appears. Of interest is the difference between o-hydroxybenzophenone, which is a good UV stabilizer, and its p-hydroxyderivative, which acts as a photosensitizer.

The o-hydroxybenzophenones are able to form hydrogen bonds. On irradiation they undergo internal changes associated with singlet and triplet states, which can be explained by the following equations:



Fluorescence and heat emission are associated with these changes, and the structure returns to its initial pattern. The triplet state has a very short lifetime (10^{-8} s),[344] which may explain the light-fastness of these compounds.

Returning to the differences between ortho and para isomers, it has been confirmed[341] that it is not the para-hydroxy group that is responsible for photosensitizing but the lack of an o-hydroxy group, since 2,4-dihydroxybenzophenone is also a good stabilizer.

The effectiveness of these stabilizers correlates favorably with the NMR hydroxy proton shift, and the higher the absolute value of the proton shift, the better the effectiveness of the 2-hydroxybenzophenone derivative.

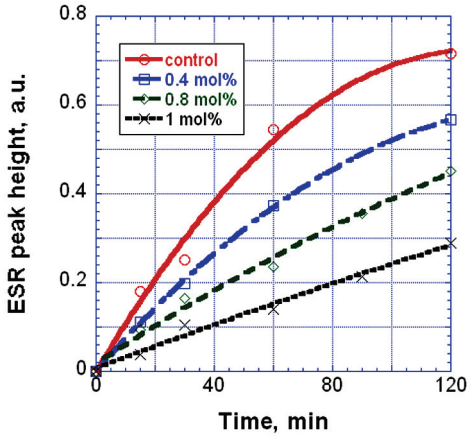


Figure 11.41. The relative ESR peak height of PVC films containing varying amounts of 4-methoxy-2-hydroxybenzophenone versus the irradiation time. [Data from Torikai, A.; Tsurata, H.; Fueki, K., *Polym. Photochem.*, **2**, 227, 1982.]

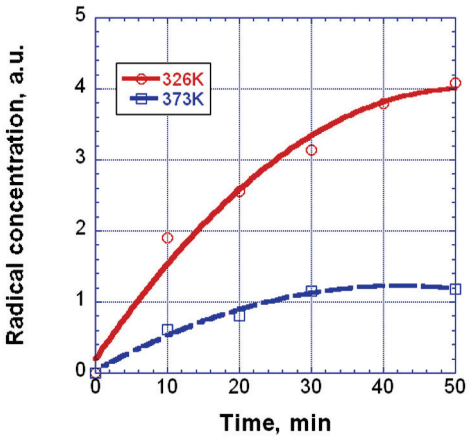


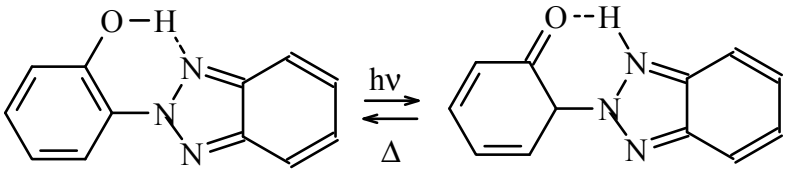
Figure 11.42. The temperature effect on radical concentration versus irradiation time. [Data from Torikai, A.; Tsurata, H.; Fueki, K., *Polym. Photochem.*, **2**, 227, 1982.]

Torikai[345] reported that the intensities of radicals decrease with an increased concentration of 4-methoxy-2-hydroxybenzophenone, which can be seen from Figure 11.41. It should be noted that temperature also affects radical concentration (Figure 11.42).

The decay rate of the radical is faster at higher temperatures. Under practical conditions of photodegradation, materials are usually exposed to temperatures higher than ambient because of the intensive transfer of energy by radiation.

By monitoring the IR spectra of irradiated samples, it was found that the concentration of UV absorber diminishes with the irradiation time. It has been suggested[345] that the abstraction of the hydrogen atom involved in hydrogen bonding, essential for the functioning of UV stabilizers, is the reason for the gradual decrease of absorber activity in the PVC product. It is thought[346] that some 2-hydroxybenzophenones may have quenching ability.

Detailed investigation of benzotriazoles has shown that they have the following resonance structures:[341]



Benzotriazoles with an o-hydroxy group show two absorption peaks, whereas those with a p-hydroxy group show only one, as in the case of benzophenone derivatives. Its photostabilization mechanism is explained by tautomerism of excited forms.[347-349]

The role of tautomeric forms in stabilization indicates the participation of the o-hydroxy group in the process of energy dispersion. The mechanism based on tautomeric

structures also indicates that the initial structure could eventually be recovered. This means that stabilizer can resist excitation and, therefore, can have long-lasting stability, unless it undergoes some other chemical changes.

With time, benzotriazole activity also decreases, although it is still the most durable UV stabilizer. It has been proposed that benzotriazoles might react with peroxyradicals which is thought to contribute to the reduced activity of benzotriazoles.[350-352] According to Hrdlovic,[346] benzotriazoles exhibit the highest quenching activity among popular UV stabilizers.

More information on the principles of UV absorption and stabilization mechanisms can be found in a book on the subject of polymer weathering.[63]

11.3.6.1.3 Costabilizers

Hindered amine liquid stabilizers, HALS, antioxidants, and pigments (carbon black, titanium dioxide, zinc oxide) are the major costabilizers discussed in separate sections. Also some thermal stabilizers have influence of PVC stability on exposure to outdoor environments.

11.3.5.1.4 Research findings

A large number of commercial UV absorbers may suggest that they are in common use in PVC stabilization, which is not the case. It is noticeable that there are about 15 main chemical products which are manufactured by several companies because their patents expired many years ago. Also, these UV absorbers are not PVC specific but are used for some other polymers since they cover quite a broad spectral range suitable for protecting many polymers.

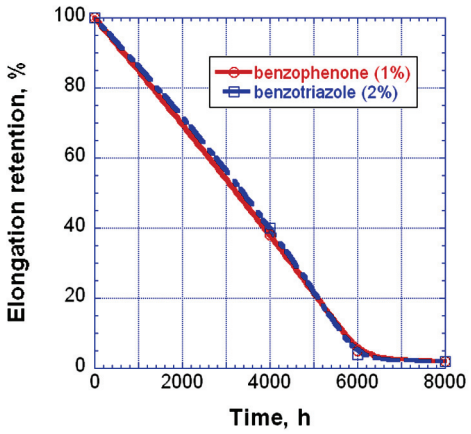


Figure 11.43. Elongation of PVC membrane vs. exposure time in Weather-Ometer. [Data from Capocci, G.; Hubbard, M., *J. Vinyl Additive Technol.*, **11**, 3, 91-94, 2005.]

The list of products suggests that the majority of protected materials has a small thickness, high flexibility, and they cannot be effectively and economically protected by other means. The bulk of PVC production is protected by titanium dioxide (see the next section).

Roofing membranes are the most challenging application for UV absorbers.[129,353] Figure 11.43 shows that UV absorbers from the most frequently used groups do not preform well, when added to the bulk.

Transparent articles constitute the other challenging group of PVC products to be stabilized against UV. In protecting properties of such films, very high concentrations (3%) of benzotriazole type UV absorber were used.[354]

Studies of building products show that Tinuvin P (UV absorber which was frequently used in the past) is not adequate to avoid or to minimize the formation of oxidation products resulting from the combined action of light and temperature.[355] Tinuvin P in

combination with Ca/Zn stabilizer improved UV resistance but half of the original impact strength was still lost after 4478 hours in a Weather-Ometer.[356]

Combinations of phenyl salicylate and maleimides were used to protect PVC products. The equimolar concentrations were the most suitable.[357]

Decker addressed a very essential question for stabilization of PVC and other polymers.[358] In stabilization of many products, two options are usually available, which are either bulk addition of UV absorber or surface coating with a formulation containing UV absorber in more durable polymer. Decker compared efficiency of both approaches to PVC stabilization.[358]

The following equations were used to calculate light absorbed by polymer:[358]

in the neat polymer:

$$I_P = I_0(1 - e^{-2.A_p}) \qquad [11.51]$$

in the bulk stabilized polymer:

$$I_{PS} = I_0(1 - e^{-2.3(A_p + A_s)}) \times \frac{A_p}{A_s} \qquad [11.52]$$

in the surface coated PVC:

$$I_{PC} = I_0(1 - e^{-2.3A_p}) \times e^{-2.3A_s} \qquad [11.53]$$

where:

I_P, I_{PS}, I_{PC}	intensity of light absorbed by PVC,
I_0	intensity of incoming radiation,
A_p	UV absorbance of PVC,
A_s	UV absorbance of stabilizer.

The filtering efficiency, S, of UV absorber in each case is given by the following equations:

$$S_{bulk} = \frac{I_P}{I_{PS}} = \frac{(1 - e^{-2.3A_p}) \times A_s}{(1 - e^{-2.3(A_p + A_s)}) \times A_p} \qquad [11.54]$$

$$S_{coated} = \frac{I_P}{I_{PC}} = e^{2.3A_s} \qquad [11.55]$$

In transparent PVC (90% transparency), $A_p = 0.043$, with stabilizer absorbing 90% of incident UV light, $A_s = 1$. Substituting these values to equations [11.54] and [11.55] we obtain $S_{bulk} = 2.5$ and $S_{coated} = 10$, which means that coating is four times more effective.[358] The efficiency of coating can be increased to 20 times of bulk addition if the amount of stabilizer is doubled ($A_s = 2$ when 99% of the incident light is absorbed).

The above calculations show that use of surface coatings is substantially more effective and also very cost efficient. UV absorbers are expensive and their use, even at very high concentrations in coating, is substantially decreased. This is one factor that decides

that many products are protected by surface coating. Automotive paints are the most well-known example of protection of paint by surface coating with a transparent layer of UV protective coating.

11.3.6.2 Inorganic UV absorbers

11.3.6.2.1 Properties and applications of commercial stabilizers

Table 11.22. Properties and applications of inorganic UV absorbers

Manufacturers: numerous manufacturers of carbon black and titanium dioxide (see monograph)[377]			
Chemical names: carbon black, titanium dioxide			
CAS#: 1333-86-4, 13463-67-7		**EC#**: 215-609-9, 236-675-5	
Mol. weight: 12-79.9	**Melting**, °C: 1825 (TiO_2)	**Boiling**, °C: 3000 (TiO_2)	**Ref. index**: 2.6 (TiO_2)
Density, 20°C: 1.7-4.2	**State**: powder	**Color**: white and black	**Odor**: none
Water solubility, %: insoluble		**Solubility in solvents**, %: insoluble	
ACGIH, mg/m^3: 3-3.5	**OSHA**, mg/m^3: 3.5 (carbon black) 15 (TiO_2)		
Composition: TiO_2 91-99.5%, SiO_2 0.15-1.1%, Al_2O_3 0.3-3.9; C 95-99%			
Exceptional properties: TiO_2: high refractive index, possible transparency (nanoproducts), surface modification with various doping imperfections which decrease catalytic influence on photodegradation; carbon black: surface modification with chemically active groups			
PVC processing methods: all (either as stabilizer or pigment)			
Product applications: window profiles, pipes, siding, wire & cable and many other products			
Recommended addition rates, phr: 0.5 to 10			

11.3.6.2.2 Mechanisms of action

Titanium dioxide performs two functions: radiation screener and additive which catalyzes degradation of PVC. Figure 5.26 shows the mechanism of degradation.

The high optical density of the film, arising from absorption/scattering by TiO_2 particles, substantially constrains the photoexcitation of electron-hole pairs (process 1) to the illuminated side of the film.[360] The low diffusion length of hole, h^+, minority carrier (0.1–1 μm in single crystal TiO_2) constrains the photoanodic process (2) proximal to the site of photoexcitation.[360] The lifetime and mobility of the electron, e^-, majority carrier are sufficient to allow long range percolation and the cathodic processes (3) and (4) can occur on both sides of the membrane. PVC oxidation is the primary photoanodic reaction caused by TiO_2. Reactions (2) and (4) show the importance of a sufficient supply of water and reaction (3) of a sufficient supply of oxygen. If conditions of exposure will restrict oxygen or water supply, the results of exposure will be proportionally changed.

In an alternative reaction, an electron combines on the surface with oxygen and forms a very reactive superoxide ion which causes peroxide formation:[361]

$$e^- + O_2 \text{ (surface)} \rightarrow O_2^{-\circ}$$

Titanium dioxide is usually doped with other metals to change its catalytic properties. The overall catalytic activity depends on several factors, such as dopant concentration, the energy levels of dopants within the lattice, the dopant's d electronic configuration, and the distribution of dopant.[361] The photoactivity also depends on the other factors, such as: particle size distribution, surface area, acid/base properties, type of pores present, amount of adsorbed reactant species and the different levels of hydroxylation of the surface.[361]

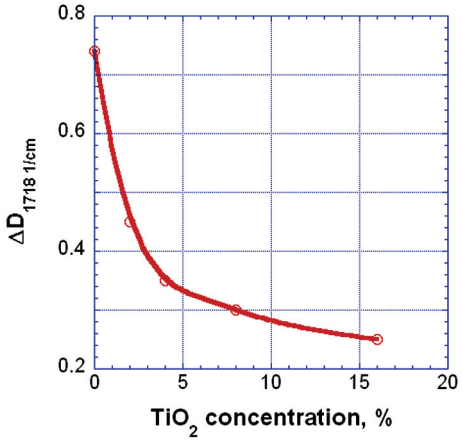


Figure 11.44. Carbonyl absorption in PVC containing variable concentrations of TiO_2. [Data from Gardette, J.-L.; Lemaire, J., *Polym. Deg. Stab.*, 33, 77-92, 1991.]

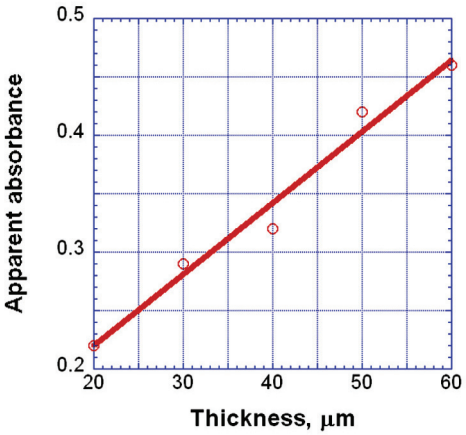


Figure 11.45. Apparent absorption of UV radiation by PVC film containing 2% TiO_2 vs. its thickness. [Data from Cho, S.; Choi, W., *J. Photochem. Photobiol., A: Chem.*, 143, 221-228, 2001.]

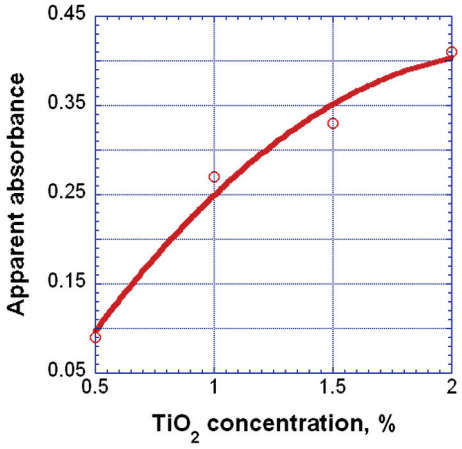


Figure 11.46. Apparent absorption of UV radiation having wavelength of 350 nm by PVC film having thickness of 50 μm vs. concentration of TiO_2. [Data from Cho, S.; Choi, W., *J. Photochem. Photobiol., A: Chem.*, 143, 221-228, 2001.]

Worsley and Searle[362] developed a test which permits measurement of photocatalyzed degradation in the presence of a particular grade of titanium dioxide. In this test, PVC pigmented with 50 wt% titanium dioxide is exposed to radiation at 365 nm and CO_2 evolution is monitored by FTIR. A photoactivity index of titanium dioxide can be determined within 6 h.[362]

The protection of the polymer by TiO_2 against UV light is a physical effect and it does not depend on its photolytic influence but rather on its dispersion.[187]

Figure 11.44 shows the effect of TiO_2 concentration on the kinetics of formation of carbonyl groups.[363] Figure 11.44 shows that the relationship follows the law of diminishing returns.

Figure 11.45 shows that absorption of radiation at 350 nm forms linear relationship with film thickness.[364] Figure 11.46 shows that the absorption of radiation increases with concentration of TiO_2 increasing.[364]

A question arises as to what concentration of TiO_2 is sufficient to protect PVC. First of all, it should be mentioned that surface layers are not protected and even the opposite is the case, because surface layers degrade under the influence of radiation and catalytic sur-

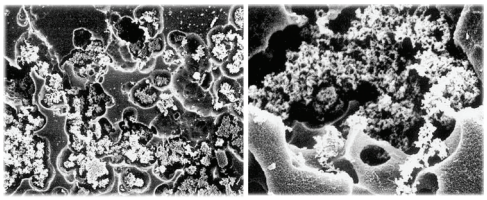


Figure 11.47. SEM images of PVC film containing titanium dioxide irradiated for 100 h. Left photograph has 10 times smaller magnification. [Adapted, by permission, from Cho, S.; Choi, W., *J. Photochem. Photobiol., A: Chem.*, 143, 221-228, 2001.]

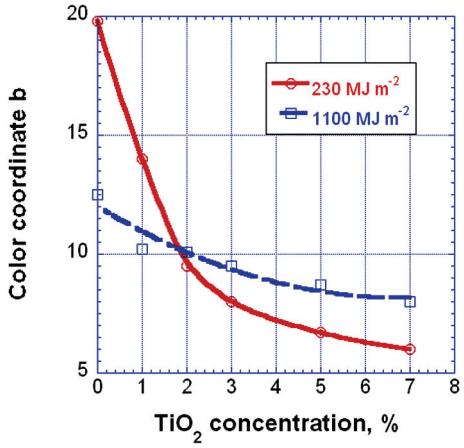


Figure 11.48. Color change on exposure to different irradiance levels vs. titanium dioxide concentration. [Data from Burn, L. S., *Polym. Deg. Stab.*, 36, 155-167, 1992.]

face of pigment. The selection of concentration of pigment is determined by requirements to balance color and rate of surface erosion. In window grade in Europe, which was stabilized by Ba/Cd/Pb stabilizers, a typical concentration of TiO_2 was 4 to 7.6 phr.[365] In the USA, where tin stabilizers were used, typical concentrations of TiO_2 were even higher (not because thermal stabilization was inferior but because of more stringent requirements of preventing color formation to satisfy customers).

Figure 11.47 shows the first stage of degradation which has removed from the surface a layer of organic material (PVC and additives) and exposed pigment which is loosely attached to the matrix because the matrix in surrounding has also been burned out. Figure 5.27 shows the next stage in which particles of titanium dioxide have been partially lost and a new surface has been exposed to radiation. Figure 11.48 shows the reasons for applications of this process. Exposure to UV radiation produces polyenes which change color to yellow and to red. Presence of photolytic pigment degrades polyenes by oxidation and eliminates color.

The effect of water is included in the description of mechanism discussed above. Samples of PVC, window grade, were exposed in a Weather-Ometer to radiation with water spray and to radiation alone. The samples exposed without water were yellow-brown and samples exposed with water were white. This experiment shows the importance of water in testing.

A similar test which was used to determine catalytic activity of titanium dioxide towards PVC[362] can be used to determine effect of pigments on photooxidation of plasticizers.[369]

11.3.6.2.3 Other findings

Carbon black applications are limited for two main reasons: color and difficulties with incorporation. Carbon black gives good protection to many polymeric materials including PVC. In plasticized PVC it requires a large amount of plasticizer for dispersion and therefore it is not frequently used. It was mentioned in one application that carbon black was not used because it was incompatible.[370] Compatibility was found to depend on surface

oxidation (the more surface oxidation, the lower the compatibility).[371] Some products are routinely protected against effect of UV by carbon black and these include pipe[190] and wire and cable.[372,373] Typically, small concentrations (0.5 to 0.8 phr) are sufficient to give good protection.

More information on application of carbon black can be found in the monographic sources.[63,359]

It is interesting to mention that PVC sheet containing titanium dioxide mounted in billboards was used for catalytic destruction of airborne VOC, such as benzene and toluene.[374] The oxidation rate on PVC sheet using natural sunlight for benzene and toluene was around 50% and 68% of that of artificial UV light.[374] This shows the extent of catalytic influence of titanium dioxide.

Carbonyl and polyene groups were generated on the surface of PVC after 480 h in QUV but incorporation of TiO_2 into PVC inhibited the number of these groups as compared to PVC without TiO_2.[375] Simultaneous chain scission and crosslinking occurred in PVC without TiO_2, but only chain scission in PVC containing TiO_2.[375]

11.3.6.3 Hindered amine light stabilizers, HALS

11.3.6.3.1 Properties and applications of commercial stabilizers

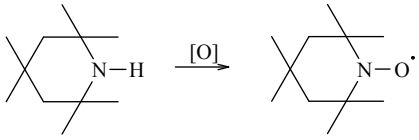
Table 11.23. Properties and applications of hindered amine light stabilizers

Manufacturers: BASF, Addivant, Clariant, Dover, Quimicoplasticos			
Commercial names: Uvinul 3434C, 4050 H, 4077 H, 4092 H, 5050 H, 5062 H; Lowilite 62, 62 granular microfine, 62 flakes, 62 NDB, 77, 77 NDB, 77 micropellets, 92; Hostavin 3051, 3055 LIQ, 3058 LIQ, N 392, VSU P; Tinuvin XT 200, XT 833			
Chemical names: monomeric sterically hindered amine, oligomeric sterically hindered amine, sterically hindered amine ester			
CAS#: 41556-26-7, 52829-07-9, 65447-77-0, 71878-19-8, 85099-51-0, 104810-48-2, 129757-67-1, 152261-33-1, 202483-55-4		**EC#**: 258-207-9, 255-437-1, 400-580-9, 406-750-9	
Mol. weight: 370-31000	**Melting**, ºC: -40 to 86	**Boiling**, ºC: >350	**Flash point,** ºC: 92->250
Ref. index: n/a	**Density**, 20ºC: 0.95-1.22	**Viscosity**, mPas: 60-6410	**Vapor pres**., Pa: n/a
Thermogravimetric analysis: from 0.4% at 150ºC, 0.7 at 175ºC, 1.3 at 200ºC, 13.8 at 250ºC to 5% at 310ºC, 10% at 322ºC, 25% at 337ºC			
State: solid and liquid	**Color**: white to yellow	**Color (Gardner)**: 4	**Odor**: odorless
Water solubility, %: <0.01		**Solubility in solvents**: acetone, ethanol, toluene	
ACGIH, mg/m^3: 3	**OSHA**, mg/m^3: 15	**LD50, rat**, mg/kg: >2000	**log Kow**: n/a
Biodegradation:		**Fresh water fish**: 96-h, mg/l: >100 to >2500	
Daphnia magna: 48-h, mg/l: 20-132		**Algae**, 72-h, mg/l: >100	
Exceptional properties: does not affect inherent color of polymer, easy incorporation, compatible with other additives, low volatility, thermally stable, minimal migration, high resistance to extraction			
PVC processing methods: calendering, coating, extrusion, injection molding, spinning, tents, tarpaulins, awnings, flooring, outdoor furniture, automotive interior and exterior, signs and banners			
Product applications: thin parts, film, fibers, rigid PVC, roofing, geomembranes			
Recommended addition rates, phr: 0.1 to 3			

11.3.6.3.2 Mechanisms of action

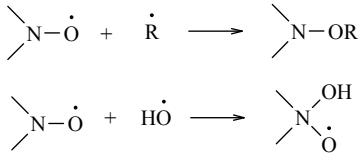
Multidisciplinary efforts resulted some time ago in the development of a series of new stabilizers based on hindered amines. They are usually called HALS (for hindered amine light stabilizer) and include numerous commercial and patented compounds.

The single most important feature of HALS is its ability to form stable radicals always available in the materials that participate in reactions and lead to increased stability. Stable nitroxyl radicals are formed during the oxidation process:



Under some conditions, they behave like free radicals. Their stability is very important because it means that they will not abstract hydrogen from polymer molecules – a

reaction which could lead to chain processes. At the same time, they are reactive towards free-radicals as the following reactions show:



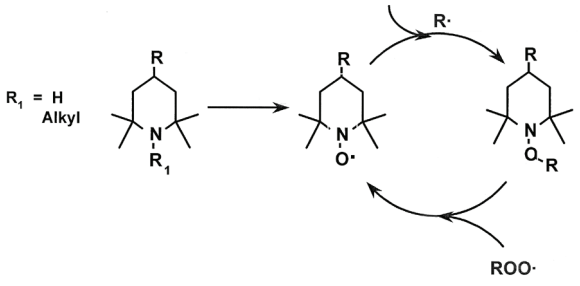


Figure 11.49. Denisov's cycle.

These reactions deactivate free-radicals and contribute to the increased stability of polymers because they break the chain reaction process. HALS stabilizers are believed to operate according to the so-called Denisov's cycle (Figure 11.49). The Denisov's cycle suggests that HALS is not used in the process of scavenging radicals but it can be regenerated and used again within the cycle. In reality, HALS stabilizer may not be exhausted because of chemical breakdown but it is frequently lost due to migration to the surface and its removal by various means, such as evaporation, reaction with other chemical materials (in the case of PVC with HCl), mechanical, and/or extraction.

These reactions deactivate free-radicals and contribute to the increased stability of polymer because they break the reaction chain process.

Depending on the group attached to the nitrogen atom HALS varies in basicity. In order for HALS to perform its basicity should be synchronized with the basicity of the material to be protected. A basic HALS should be used with a basic material and *vice versa*. Acid components in the material (such as HCl) will interact with basic HALS to hinder its performance. It is also essential to determine if the selected HALS is compatible with the matrix. A variety of HALS with varying solubilities in different materials are available but none is as acidic as PVC. For this reason HALS was not frequently used in PVC.[129]

There is some hope that the so-called NOR HALS (manufactured under the name of Tinuvin XT 833) will give expected performance. It is less basic than typical HALS and not so reactive with HCl. Figure 11.50 shows its performance in roofing membranes which is the most challenging application for UV stabilizers.[353] There is substantial improvement compared with UV absorber but degradative processes are still causing substantial damage to the mechanical performance of the membrane.

It is important to have performing HALS stabilizer in a formulation because, in addition to other functions, HALS protects UV absorber from degradation. If surface coating is used for protection of PVC articles, UV absorber must perform well and for a long time

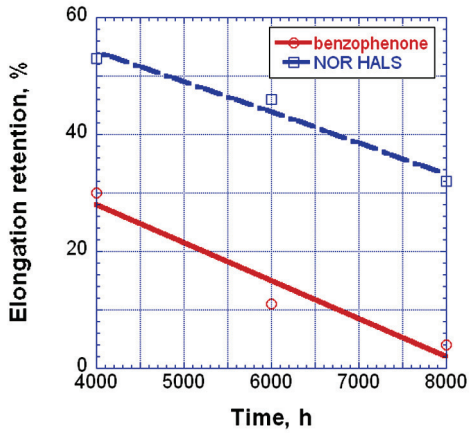


Figure 11.50. Elongation retention of PVC membrane containing 1 phr stabilizer vs. time of exposure in Weather-Ometer. [Data from Capocci, G.; Hubbard, M., *J. Vinyl Additive Technol.*, **11**, 3, 91-94, 2005.]

to prevent penetration of UV radiation inside, beyond coating, and inside the PVC layer.[358]

There is an interest in the application of HALS in the patent literature. Light-stable fluorescent PVC articles have been developed for highway roll-up signs.[376] Polymeric HALS was used in the application.[376] Stabilizer combination was developed for articles performing outdoors.[377] The composition includes zinc compound, another metal compound (e.g., Al, Mg, Na, or K), and sterically hindered amine.[377] Many new sterically hindered amine stabilizers were developed. One such group includes amine ethers, which are suitable for PVC stabilization.[378]

It should also be pointed out that monomeric, oligomeric, and polymeric HALS are used. The molecular weight has a bearing on stabilizer retention but it also influences its rate of migration to the site where reaction with radicals is required. There is need for the balance of these two properties. Sometimes appropriate balance is achieved by mixing two or more different HALS products.

11.3.7 LUBRICANTS

11.3.7.1 Properties and applications of commercial lubricants

Table 11.24. Properties and applications of lubricants

Manufacturers: Baerlocher (as an example) and numerous other manufacturers			
Commercial names: Baerolub L-AK, LAS, LS 100, FTA, PA, L-PL, L-MS, L-TP;			
Chemical names: amide wax, stearic acid, complex ester, oxidized polyethylene wax, partial ester of glycerol, phthalate ester			
CAS#: 57-11-4, 110-30-5, 123-95-5, 1592-23-0, 68441-17-8		**EC#**: 200-313-4	
Mol. weight: 284-6000	**Melting**, °C: 46-160	**Boiling**, °C: 218-383	**Flash point,** °C: 113-200
Density: 0.85-1.09	**State**: solid	**Color**: white o off-white	**Odor**: odorless to fatty
Water solubility, %: insoluble		**LD50, rat**, mg/kg: 4640-32000	
ACGIH, mg/m^3:	**OSHA**, mg/m^3:		**log Kow**:
PVC processing methods: blow molding, calendering, dip molding, extrusion, injection molding, rotational molding			
Recommended addition rates, phr: 0.05-3.5			

11.3.7.2 Mechanisms of action

Figure 11.51 shows various models of friction. All these types of friction are applicable in polymer processing. The most important for PVC processing are the types of friction shown by diagrams a and d. In the case of internal friction, cohesion forces between the particles of material and the influence of various additives on these forces are of interest. In the boundary-layer friction (usually called, in PVC processing, external friction), the character of the metal surface, the type of liquid forming the boundary layer, and interactions between boundary-layer material and metal or between boundary-layer material and polymer are of major concern.

Let us discuss these elements of total friction phenomena one by one. The character of the metal surface in contact with either polymer or lubricant is important, not only for the processing conditions of polymer, but also for the durability of machinery, which is an equally important factor in industrial economy. The surface layer of the metal is a critical factor in several processes, which can be grouped as follows:

- mechanical changes: stress formation in crystallites, deformation of crystallites, loss of material particles,
- thermal changes: heat formation, changes in temperature distribution, thermal relaxation of material,
- physico-chemical changes: adhesion, adsorption, diffusion, chemical reactions.

For a chemist, the last two groups of changes are the most important. Friction between the boundary layer and the surface layer of the metal depends, first of all, on the actual character of the metal. The following geometric features of the surface are differentiated:

- macroscopic – shape, arrangement,
- microscopic – surface roughness,
- submicroscopic – submicroscopic surface roughness.

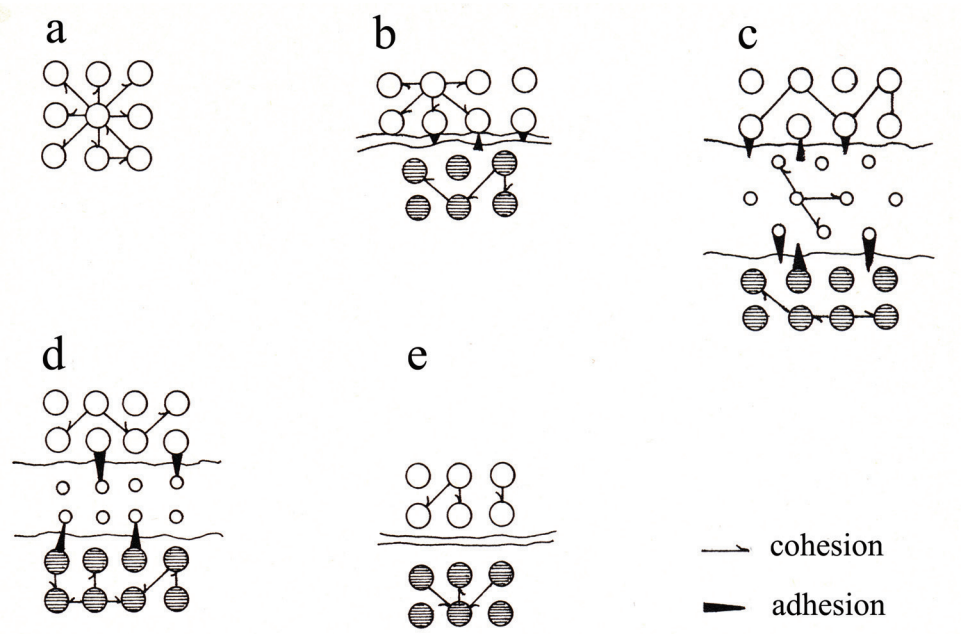


Figure 11.51. The models of various types of friction: a.) internal friction; b.) external friction; c.) liquid friction; d.) boundary-layer friction; e.) dry friction.

On the macro-level, the character of the metal surface depends on the thermal process of metal formation and finishing. We also need to account for atmospheric conditions and conditions of use, which affect the initial state of the surface (e.g., HCl corrosion). On the metal surface, layers are formed that are bound by physical forces (adsorption of gases) and chemical forces (layers of oxides, chlorides, sulfates, hydroxides, etc.)

From the above explanations we can draw at least two important conclusions. First, under such conditions we cannot expect to find a general solution for the lubrication problem, since practically every machine needs special attention. Secondly, we must understand that no condition is permanent, and throughout the duration of machinery use, some adjustments are needed to balance the damage done to the equipment. These problems of internal-external lubrication, so simple on the surface, call for considerable expertise to solve the lubrication problem as it relates to the economy of production, durability of equipment, and product quality.

The first fundamental studies on the theory of lubrication, using hydrocarbons and fatty acids as models, were set out at the beginning of the 20th century by Hardy.[379,380] Some of his findings, still valid today, concern the relationship between the friction coefficient and the molecular weight of n-paraffins, fatty acids, and alcohols. With an increase in the molecular weight of the lubricant, the friction coefficient decreases. Hardy used Langmuir's theory of adsorption to explain formation of a layer of adsorbed molecules.

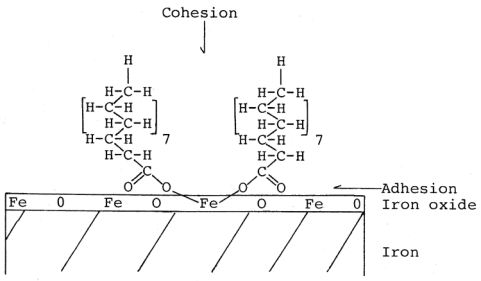


Figure 11.52. Godfrey's model of chemisorption of stearic acid on iron surface. [Modified from Godfrey, D., in Lubrication and Wear, Proc. Int. Symp. Lubrication and Wear, Berkeley, 1965].

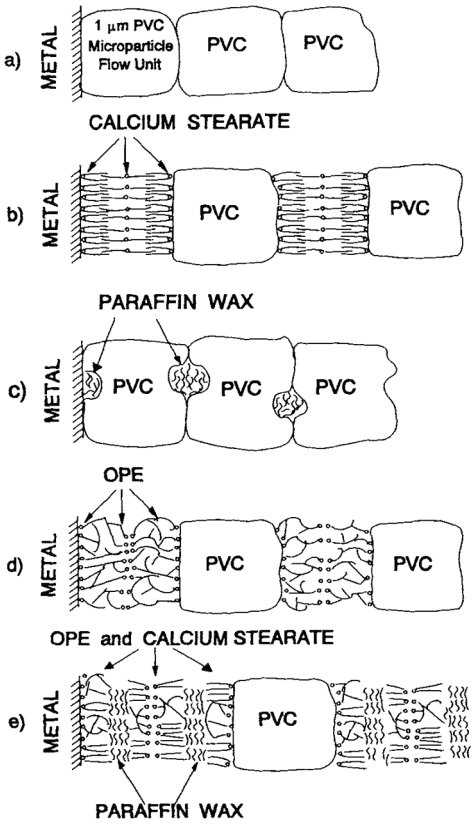


Figure 11.53. Model of PVC lubrication. [Adapted, by permission, from Chen, C. H.; Wesson, R. D.; Collier, J. R.; Lo, Y. W., *J. Appl. Polym. Sci.*, **58**, 7, 1107-15, 1995.]

Bowden[381-383] corrected Hardy's conclusions and showed that the relationship between molecular weight and the friction coefficient is correct only in a certain range (in the case of fatty acids, up to 120); above the upper limit of that range, the friction coefficient has a constant value.

Bowden, analyzing the effect of temperature on the lubricating properties of fatty acids and alcohols, found that temperature increase is accompanied by only slight changes in the friction coefficient up to a certain temperature limit; after that, a rapid increase is observed. For paraffins and fatty alcohols, this rapid change of the friction coefficient is usually at the melting point but in the case of fatty acids it is far above the melting point, which means that fatty acids are adsorbed more than alcohols and paraffins. If the same studies for fatty acids are repeated with non-reacting metals, such as gold or platinum, the rapid change is at the melting point of fatty acids. These observations led to the assumption that fatty acids may react with metals to form soaps. If it is true, the boundary layer is formed rather by metal soap, which has a higher melting point.[384]

Based on experimental results, Godfrey[385] proposed the model of adsorption of polar hexadecanol and stearic acid on a metallic surface as shown in Figure 11.52. Similar models of adsorption of tricresyl phosphate and stearic acid have been proposed by Vinogradova.[386]

Rabinovitch *et al.*[387] discussed the mechanism of lubrication in PVC which is explained in Figure 11.53 in a version modified by Chen *et al.*[388] The polar ends of calcium stearate molecules adhere not only to the polar PVC but also to the polar metal surface, leaving the nonpolar tails to bring about the lubrication (Figure 11.53b). Cal-

cium stearate displaces PVC melt from the metal surface, preventing it from sticking and providing limited slip between the metal and PVC melt surfaces.[388] The polar groups in calcium stearate are also attracted by each other, which causes formation of a viscous layered structure. Oxidized polyethylene, OPE, is also polar. Therefore, the carboxylic groups of OPE attach to a metal surface, to the surfaces of a PVC particles, and to each other, as well (Figure 11.53d).[388] Paraffin wax is a nonpolar, straight-chain hydrocarbon with a lower surface energy than that of PVC. It does not preferentially wet the metal surface and does not displace the more polar PVC microparticles. If paraffin wax is used alone, PVC sticks to the metal surface (Figure 11.53c). If calcium stearate and paraffin wax are used together, interaction between the tails of calcium stearate molecules is hindered by the presence of mobile, nonpolar paraffin wax molecules.[388] Paraffin wax molecules are neither attracted to the polar groups of calcium stearate, to PVC, nor to metal surface, but they are weakly attracted to themselves and the nonpolar hydrocarbon tail of calcium stearate molecules (11.53e).[388] No fusion occurs when medium temperature is used, which may be due to a mobile layer that increases separation and slipping among PVC particles.[388] At higher temperature, this mobile layer may be destroyed and particles will be fused together.[388]

From the above discussion, one can see that a stabilized layer of a lubricant may form that isolates polymer from direct contact with a metal surface. In the case of polymer processing, the boundary layer works under steady conditions as friction and polymer mass flow tend to remove it mechanically from the metal surface. Therefore, a state of equilibrium has to be achieved in which fresh portions of material carrying the lubricating agent are able to release it easily to allow the lubricant to function continuously.

Discussion of lubricant action includes two different concerns: the phenomena resulting from contact between the polymer mass and parts of the machinery, and internal friction within the material.

We expect that the flow of polymer close to the surface of other material will be relatively steady, and adhesion to metal surfaces of high temperature will be regulated. One might suggest that the adhesion could easily be solved by coating the surface of the material with a substance having a very low friction coefficient. But such an action, even if technically feasible, is not adequate, as we need internal friction in the material to achieve fusion. Viscous internal friction is explained by the friction of material layers of relatively different rates of flow; therefore, if the material was to move almost without restrictions against one of the surfaces, the gradient of flow (shear rate) could not be achieved.

The models in Figures 11.52 and 11.53 show in essence a “molecular brush” which serves as a boundary layer on one side and applies a reduced (or regulated by composition) friction between the surface and polymer. By regulating the properties of the “brush” (e.g., length, density, and so on), we can control external lubrication. We cannot, however, consider the boundary layer as a steady phenomenon but rather as dynamic and competitive. In contact with “the brush” there is a constant flow of material which contributes new portions of lubricant able to enrich the boundary layer but flowing material can also wipe lubricant out by mechanical force. Under given conditions, e.g., equipment geometry, rate of material flow, temperature and composition, we may expect to achieve a state of equi-

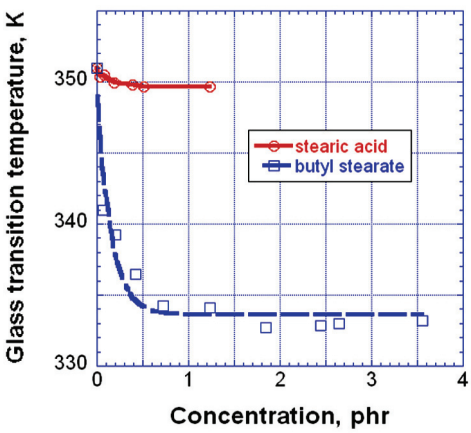


Figure 11.54. The effect of stearic acid and butyl stearate on glass transition temperature. [Data from Ceccorulli, G.; Pizzoli, M.; Scandala, M.; Pezzin, G.; Crose, G., *J. Macromol. Sci.-Phys*., **B20**, 519, 1981.].

librium in the processing conditions which can be changed only when one of the parameters of the process is affected.

The concentration of lubricant at interface and its orientation requires discussion. It was reported[390,391,392] that the increase in chain length proportionally decreased the compatibility of lubricant in resin. Worschech[389] compared lubrication using alcohol having C16-18 with that of C22 and the fusion times were 4.6 and 7.3 min., respectively. The performance did not depend on chemical structure but only on the length of carbon chain, for example, lauryl stearate (C17) and stearyl laurate (C18) gave fusion times of 5.5 and 6.0 min, respectively. Extension of the length of the carbon chain improves its release from the polymer mass (it lowers compatibility), which subsequently increases the amount lubricant in the boundary layer. External lubricants have longer carbon chains than internal ones, as several authors[390,391,393,394] have pointed out.

Ceccorulli's paper[401] gives comparative data for both groups lubricants, and makes an interesting proposal for the study of lubricant compatibility. Figure 11.54 shows the effect of two lubricants on the glass transition temperature. Stearic acid, an external lubricant, is compared with butyl stearate, an internal lubricant. Whereas the first has almost no effect on the glass transition temperature, the other plays an important role. Another observation of importance is that the method used to incorporate lubricant into the mixture affects its performance because of its distribution.

Ceccorulli[401] also shows ways of measuring the parameters of Flory-Rehner's equation which can, therefore, be applied for interpretation of an interaction of partially soluble additives with PVC. The method has not been investigated sufficiently, but the results already presented indicate that it may be a useful tool for studying lubricants.

Fisch and Bacaloglu[88] developed classification of lubricants based on their IR absorption and their effect on the glass transition temperature (see Figures 11.10 and 11.14). Based on characteristic infrared absorption bands they were able to divide carboxylates of various metals and carboxylic acid to the following groups:

- ionic – Li, Na, Ca, and Ba,
- covalent bidentate chelating – Ca and Zn,
- covalent bidentate bridging – Li, Mg, and Al,
- covalent unidentate – CH_3 and Al,
- associated chelating – stearic acid.

Infrared absorption was related to their interaction with PVC and the nature of interaction with PVC had bearing on the glass transition temperature of mixture with PVC.

Metal carboxylates, which had a small influence on the glass transition temperature (below 2°C), did not have strong interaction with PVC and were able to exude more freely to the surface, and these are termed conventionally as external lubricants. This group includes stearic acid, magnesium stearate, and zinc stearate. Metal carboxylates, which have strong interaction with PVC, had stronger influence on the glass transition temperature and these are the lubricants which were considered to "dissolve" in polymer and act as internal lubricants. This group includes calcium stearate, barium stearate, and also methyl stearate. Some carboxylates are borderline, such as sodium stearate and aluminum stearate and they have both internal and external properties at their saturation concentration. The amount of added lubricant also influences the character of action of lubricant. If internal lubricant is added at a concentration higher than its saturation concentration, then its excess will act as external lubricant.

The above results show that both aliphatic chain and interacting group influence lubricating properties.

For a good performance, it is also essential that the polar groups can be properly oriented towards the surface and interact with metal. One should not be misguided by the fact that in lubrication of polymers we use substances such as hydrocarbons and polyethylene waxes, which do not contain polar groups. Godfrey[385] suggested that links have been formed by hydrogen bonding. Worschech,[389] who studied three linear diol esters of the same total length of 38 carbon atoms, found that when the distance of the polar centers was increased (unfortunately, at the same time the carbon chain length was decreased), lubricating properties were reduced. Worschech explained this phenomenon by increased solubility, but one wonders if structure does not play a role here, as one can suppose that if any links are formed with the metal surface, it is much easier to do so with a compound having a very short carbon chain (e.g., C2) that isolates two polar groups.

Worschech has also found that increased doses (above 0.5 phr) of lubricants, regarded as external, influence the internal lubrication system, as well. This finding was also confirmed by Guignard[395] and Riethmayer,[396] who mentioned that stearic acid in doses up to 0.5 phr behaves as an external lubricant, whereas when its amount is increased, it starts to exhibit the properties of an internal/external lubricant. These observations seem to confirm the proposed model. At higher concentrations, stearic acid seems to fulfill the condition of saturation of the boundary layer, and its excess, which cannot be further utilized by bonding to a metal surface, is mechanically incorporated into the polymer mass, where it serves as an internal lubricant. Godfrey[385] agrees that in selecting the external lubricant, one tends to choose a substance of higher affinity to the metal surface. Furthermore, Pukanszky,[397] Marshall,[390] Fredriksen,[398] and Cernach[399] describe external lubricants as having affinity to a metal surface. All these findings agree with a method of recognition of lubricant properties proposed by Fisch and Bacaloglu.[88]

The essential information confirming the proposed mechanism can be found in Karpatsheva's *et al*. paper.[400] The authors analyzed glycerin monoricinoleate and glycerin in respect to retention of lubricant in the product at the beginning of the process and the effect of the pressure of extrusion on lubricant's retention. Extracting the lubricant from the final product and analyzing it by IR-spectroscopy, they detected no change in the orig-

inal material in either case. Next, they analyzed the recovery of lubricant in the product after 2, 60, and 95 mins. For glycerol monoricinoleate (internal lubricant) they found almost 100% recovery, whereas for glycerin (external lubricant), recovery was in the range of 59.5-56.0%. Also, the effect of extrusion pressure was manifested differently in both cases. An increase in pressure was accompanied by a decrease in glycerin monoricinoleate and an increase in glycerin in the final product. These results seem to support the proposed model of external lubrication.

The use of ester lubricants at significantly lower concentrations than their saturation concentrations ensured their permanence in the polymer.[402] At this range of concentration, lubricants act as internal lubricants, reducing the viscosity of the melt. If lubricants are used at much higher concentrations they reside at the surface of the polymer, giving them an external character. The efficiency constant characterizes the capability of the lubricant to modify the properties of the polymer and increase flow.[402]

Internal lubrication is far simpler to understand, at least its general character. In this case the additive should be chosen so as to regulate internal friction. The level of remaining friction is also essential as friction heat is necessary to achieve proper fusion of the material. Overlubricated material will yield a product of low mechanical strength because of incomplete fusion, whereas at the other extreme, the product may be thermally degraded. Thus, simple rheological tests cannot serve in practice, since other factors besides viscosity are essential. The actual viscosity inside the equipment depends not only on composition, temperature, pressure, the geometric shape of the equipment, and the rate of shear, but also on all parameters governing external lubrication.

White[394] suggests that the role of internal lubricant is similar to that of plasticizers and calls them pseudoplasticizers because they can reduce melt viscosity by reducing van der Waals forces between polymer chains (or particles). Their difference from plasticizers is demonstrated at the ambient temperature as they do not greatly affect the physical properties of the material. It seems probable that lubrication is mostly on the level of primary particles rather than chains (see Figure 11.54), which is also demonstrated by the relatively low viscosity of "melt."

11.3.7.3 Other findings

Minsker *et al*.[403] classified lubricants based on the viscosity and thermal stability of plastificates. Comparing the results for three common plasticizers, he found that in PVC mixtures they behaved differently than the substances usually intended as lubricants. It has been established from the beginning that the lubricant is a processing aid. Ideally, it should not affect any other parameter, such as the thermal stability of the mixture during processing and the elasticity and tensile strength of the final product. Based on this, plasticizers do not belong to the group of lubricants even if they are meant to change the viscosity of melt or plastisol, because plasticizers interact with polymer and change the rheological properties of the final material.

When lubricants are classified according to function, they are usually divided into internal and external lubricants.[404] The usual aim of external lubricant is to improve the flow of molten polymer against the metal surface.[395] Earlier discussion of the basic principles of lubrication established that the external lubricant should be easily released by poly-

mer in order to be found during processing in a readily formed boundary layer. Therefore, one should expect an external lubricant to be incompatible not only with polymer but also with the composition under consideration. Furthermore, an external lubricant should be able to interact with a metal surface, which helps to stabilize the boundary layer. Finally, based on Bowden's data,[381-384] an external lubricant should be thermally stable at the processing temperature.

Internal lubricants have an entirely different function. Their presence should affect polymer melt; to do so, they should be compatible with polymer composition, as they must decrease internal friction inside the material. This means, first of all, friction between the polymer's grains; then, after the polymer's granular structure has been destroyed in the process, friction between the primary particles must also be decreased.

Worschech[386] criticized the idea of classification of "external/internal" lubricants, as follows:

> When talking about lubricants it is almost a tradition to mention new definitions about internal and external lubricants. This means to classify also such products into a specific group which under normal circumstances are rather difficult to classify. The existence of such a general classification is not favored by us, unless all PVC producers are willing to find a basis for a standard formulation for all processes and applications. As this is virtually impossible, it is essential to find solutions about effectiveness of lubricants in each individual case as it is impossible to eliminate the influence of a lot of parameters, even if one tries to simplify.

Worschech's statement is very important not only for this particular discussion but also for interpretation and analysis of research results in general. The classification of "internal/external" lubricants serves only to characterize the nature of the physical properties desired either in research or in a particular technical solution.

The clarity of PVC provides another way to classify lubricants, as their incompatibility with PVC produces haze.[390] Generally, test formulations including internal lubricants show a clarity above 90%, whereas external lubricants are sometimes far below 90%. Calcium stearate and stearic acid fall into the group of external lubricants, but they are also viewed as internal lubricants.[391] Classification based on clarity should be used with great care because clarity might be affected by lubricant distribution. Clarity test results might also be influenced by other additives, which will affect the compatibility of the lubricant.

Other means of classification of "internal/external" lubricants are derived from measurements of the glass transition temperature of the PVC compound,[88,401,405] from measurements using a torque rheometer,[406,407] or an annular shear cell.[408,409] In the glass transition temperature measurement, highly compatible lubricants such as ethyl and butyl stearates will produce lower temperatures than calcium stearate, stearic acid, or stearyl stearate.

In the case of the torque rheometer, the longer the time taken for the torque peak to be reached (fusion time), the slower the melting rate in the extruder. In a series of experiments reported by Gale[393] with various proportions of glycerol monostearate (compatible)

and stearic acid (incompatible), the composition including only glycerol monostearate had a very short "fusion time"; but the actual sample was completely unfused. In the opposite case, for the sample of the highest concentration of stearic acid, the fusion time was the longest, but the sample was fused. Annular shear cell measurement has produced results difficult to explain, with very low resolution that does not allow for distinguishing the character of various lubricants.

Ditto[410] divides lubricants into gelation retarders and promoters and slip agents. Gelation retarders prevent premature fusion in the feed zone of an extruder, gelation promoters balance out the effect of retarders when the composition reaches the compression or mixing zone, and slip agents provide excellent release properties in the metering section and die.

Lubricants form a very large and diverse group of chemical compounds, some of which are chemically homogenous, but most of which are mixtures of components or polymerized products. The main groups of lubricants constitute the following substances: fatty acids; fatty acid salts; esters of fatty acids; fatty acid amides; fatty alcohols; partial esters (mainly glycerol monoesters of fatty acids); natural and epoxidized oils; hydrocarbons, both natural and synthetic; polyethylene waxes; benzoic acid esters; phthalic acid esters; various amides; ethers and sulfates; esters of branched and straight chain monocarboxylic acids obtained from olefins; and esters of dicarboxylic acids with multifunctional alcohols. This list is incomplete.

Lubrication is absolutely critical in the case of a rigid PVC product, whereas a flexible PVC mixture usually has enough lubrication because of plasticization. In the extreme case which occurs in plastisol coating, there is rather a need for a viscosity modifier in order to increase viscosity or to change the rheological character of flow. Obviously, one cannot make any sharp division, in this respect, as there are many processes for manufacturing flexible PVC articles in which lubricants are as crucial as they are in the processing of rigid PVC. Lubrication is most essential in the following processes: preparation of dry blends, extrusion, calendering, injection molding, blow molding, and compression molding. Some of these processes are discussed below.

11.3.7.3.1 Preparation of dryblends.

Dryblends are the most common form of material in the processing of both rigid and flexible PVC. In various processes they have replaced pre-compounded granules, which were in common use in the 1960's. Dryblend production is usually performed in high-intensity mixer and cooler combinations in which additives such as stabilizers, lubricants, impact modifiers, process aids, pigments, etc. are uniformly distributed in the polymer. This process usually involves a temperature increase up to 100-120^{o}C. The mixture is then cooled, after which it is ready for further processing. Lubricants are usually added when temperature reaches around 60^{o}C either as an entire lubrication pack or else external lubricant is added at slightly higher temperature (e.g., 70^{o}C).

The mixing temperature is relatively high, which requires lubricants having a high melting point. The melting point of the lubricant is, therefore, an important factor in deciding its applicability. The melting point of a lubricant depends not only on its chemical structure but also on admixtures present because of its production method. In conse-

quence, lubricants of the same chemical structure may vary in melting temperature by up to 30K in different mixtures.

11.3.7.3.2 Extrusion

In the case of extrusion, first consideration must be given to the type of composition to be processed. If the composition includes plasticizers, the viscosity of the melt is sharply decreased, compared with similar compositions excluding plasticizers. The shear stress during processing could, therefore, be considerably reduced without danger of overheating from frictional heat as less mechanical energy is put into the composition. Plasticizers and stabilizers incorporated into such systems are usually not sufficient to eliminate the need for lubricants. External lubricants, at least, have to be incorporated.

The other consideration relates the type of polymer processed to its behavior during processing.[401] It has been evident since fundamental studies by Berens[411-413] were published that there is a difference in melting characteristics of emulsion and suspension PVC. Individual grains of emulsion polymerizate remain unaffected under the usual conditions of extrusion, which do not influence the mechanical parameters of the final product. In this case, lubrication should assist particle slippage, which is unlike the behavior of suspension PVC, which needs more attention.

Other components of the mixture also exert considerable influence. Metal soaps, lead stabilizers, epoxides, and even some tin stabilizers may contribute to the total lubrication. Fillers affect lubrication because of the type of coating used and the grain size distribution. Fillers of small particle size usually need more lubrication, whereas small additions of fillers or coated fillers may facilitate lubrication, thus calling for a decreased level of lubricant. The same effect is expected from pigments. Antistatic agents and some biocides also contribute to lubrication.

Finally, the form of material fed into the extruder is also an essential consideration. Pelletized compounds, which are already partially or completely fused, will cause fewer fusion problems, and the level of lubricant might, thereby, be considerably reduced as compared with dry blends.

The other group of essential parameters concerns processing conditions. Temperature, pressure, and shear rate are inevitably connected with lubricant behavior. An increase in the extrusion pressure affects the compatibility of lubricants;[400] internal lubricants may became less compatible, whereas external lubricants may become more so. Extrusion temperature might greatly affect melt properties and lubricants' effect thereon, as demonstrated by Shah;[414] also, the melting degree depends on temperature.[393,411,412] Through these parameters and the construction of the extruder, lubricants are interconnected with the processability of PVC mixtures.

Considering all these parameters, it is difficult even to offer guidelines for lubricant selection, since for practically every formulation for a particular machine, the proper composition has to be developed based on laboratory tests and practical trials. Beyond that, additional problems must be considered, for example, electric insulating properties in the case of cables.[415]

11.3.7.3.3 Calendering

Calendering usually needs a higher level of lubricants than does extrusion; also, the ratio between external and internal lubricant has to be controlled and properly selected. It is easier to choose proper lubrication for calendering, as overlubrication hardly ever occurs.

Because of the structural distribution of the forces which act in calendering and extrusion, the lubrication of mixture must be evaluated differently. Close attention is needed, especially when clear sheets are produced, so that lubricants yield good roll transfer and good release, and so that clarity is not affected. Normally, fusion time or temperature depends on the amount of lubricant added.[416] Especially in calendering, where tensile strength is important, this factor should be controlled, as the mechanical properties and efficiency of production may be affected by the kind and amount of lubricant chosen for a particular PVC type.[417]

In the calendering process it is important to include external lubricants of good releasing properties called release agents. These include montan waxes, high molecular weight fatty acid esters, oxidized paraffins, polyethylene oxidates, and some metal soaps.[419] The latter do not allow production of PVC high transparency films.[418] Worschech[389] demonstrates how the lubricant level can influence film clarity. Among three tested lubricants of the phthalic acid ester type, additions of distearyl p-phthalate were critical to film clarity at doses exceeding 2 phr; fusion time of the mixture containing that lubricant was also highly prolonged. Stearic acid, paraffin, and HDPE-wax, which are all very effective in external lubrication in the extrusion process, exhibit very short sticking time when they are tested on a twin-rolls-mill, which limits their use in calendering.

11.3.7.3.4 Molding

Molding processes are more closely related to extrusion than to calendering.[393,394] High flow vinyl injection molding compounds have usually three lubricants: internal (e.g., glycerol monostearate), external (e.g., polyethylene wax), and lubricating process aid which reduces plate out.[419] Impact modifier usually increases melt viscosity and thus it requires increased amounts of lubricants.

11.3.7.3.5 Rigid foam

A range of lubricants were tested for use in rigid foam.[420] Internal/external costabilizing lubricant has increased thermal stability of material (blowing agents affect stability) and gave lower density of foam.[420] Many types of lubricants found application in rigid foam, including paraffin waxes, calcium stearate, fatty acid esters.[421] Lubricants typically control the rate of fusion and therefore the rate of heat generation.[422] This affects gas evolution since blowing agents decompose and generate gas at elevated temperatures.[422] The formulation must balance fusion characteristics and stock temperature to avoid premature gas evolution.[422] Conventional paraffin wax and calcium stearate systems used in solid, rigid PVC formulations work well in foam PVC, as do various types of ester lubricant systems.[422]

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12

Health & Safety and Environmental Impact

This chapter contains information on regulations, which are relevant for PVC use. The data characterizing severity of influence of PVC and its additives on health and safety and environmental impact are included here. The following aspects are discussed below:

- toxic substance control
- carcinogenic effect
- teratogenic and mutagenic effect
- workplace exposure limits
- exposure from consumer products
- presence in drinking water
- food regulatory acts
- toxicity of stabilizers.

12.1 TOXIC SUBSTANCE CONTROL

The United States Congress enacted the Toxic Substances Control Act.[1] The following are the premises of the Act: "human beings and the environment are being exposed each year to a large number of chemical substances and mixtures; among the many chemical substances and mixtures which are constantly being developed and produced, there are some whose manufacture, processing, distribution in commerce, use, or disposal may present an unreasonable risk of injury to health or the environment."

The chemical substances in the Chemical Substances Inventory contain chemical compounds which are permitted for the use by industry. New compounds not available on this list must undergo a process established by the Environmental Protection Agency, EPA.

The Inventory is not created to list substances but for the purpose stated in Section 2624: "The Council on Environmental Quality, in consultation with the Administrator, the Secretary of Health and Human Services, the Secretary of Commerce, and the heads of other appropriate Federal departments or agencies, shall coordinate a study of the feasibility of establishing a standard classification system for chemical substances and related substances, and a standard means for storing and for obtaining rapid access to information respecting such substances."

This very useful regulation, after more than a quarter century of practice, does not give sufficient information. EPA has selected a group of High Production Volume, HPV, chemicals which constitutes 2,863 organic chemicals produced or imported at or above

one million pounds per year in the United States. These chemicals have a large impact on health and safety because of their widespread application. EPA's analysis found in 1998 that no basic toxicity information, i.e., neither human health nor environmental toxicity, was publicly available for 43% of the high volume chemicals manufactured in the US and that a full set of basic toxicity information is available for only 7% of these chemicals.

The lack of this basic toxicity information on the most high volume chemicals is a serious issue for risk assessment, safeguarding children's health, expanding the public's right-to-know, and promoting the pollution prevention ethics which are important EPA initiatives.

Table 12.1 lists additives which are HPV chemicals and information on data availability on acute toxicity, A, chronic toxicity, C, teratogenicity, T, or developmental and reproductive toxicity, mutagenicity, M, ecotoxicity, E.

Table 12.1. PVC additives on HPV chemicals list and data availability[2]

CAS #	Plasticizer name	Data available (Y - yes; N - no)				
		A	C	T	M	E
57114	Stearic acid	Y	Y	Y	Y	Y
77907	Citric acid, tributyl ester, acetate	Y	N	N	N	N
78400	Phosphoric acid, triethyl ester	Y	Y	Y	Y	Y
78422	Phosphoric acid, tri-(2-ethylhexyl) ester	Y	Y	N	Y	Y
84617	Phthalic acid, dicyclohexyl ester	Y	Y	N	Y	N
84662	Phthalic acid, diethyl ester	Y	N	Y	Y	Y
84695	Phthalic acid, diisobutyl ester	Y	N	Y	Y	Y
84742	Phthalic acid, dibutyl ester	Y	Y	Y	Y	Y
84775	Phthalic acid, didecyl ester	Y	N	N	N	N
85687	Phthalic acid, benzyl butyl ester	Y	Y	Y	Y	Y
85698	Phthalic acid, butyl 2-ethylhexyl ester	N	N	N	N	Y
102761	Acetin, tri-	Y	N	N	N	Y
103231	Adipic acid, di-(2-ethylhexyl) ester	Y	Y	Y	Y	Y
103242	Azelaic acid, di-(2-ethylhexyl) ester	Y	N	N	N	N
108634	Adipic acid, di-(1-methylheptyl) ester	N	N	N	N	N
110292	Adipic acid, decyl octyl ester	N	N	N	N	N
110305	N,N'-ethylene bisoctadecanamide	Y	N	N	N	N
110338	Adipic acid, dihexyl ester	Y	N	N	N	Y
115866	Phosphoric acid, triphenyl ester	Y	Y	Y	Y	Y
117817	Phthalic acid, di-(2-ethylhexyl) ester	Y	Y	Y	Y	Y
117840	Phthalic acid, dioctyl ester	Y	N	Y	Y	Y
119062	Phthalic acid, ditridecyl ester	Y	N	N	Y	Y

Table 12.1. PVC additives on HPV chemicals list and data availability[2]

CAS #	Plasticizer name	Data available (Y - yes; N - no)				
		A	C	T	M	E
122623	Sebacic acid, di-(2-ethylhexyl) ester	Y	N	N	Y	N
123795	Adipic acid, dioctyl ester	N	N	N	N	Y
124265	Stearamide	N	N	N	Y	Y
126738	Phosphoric acid tributyl ester	Y	Y	Y	Y	Y
131113	Phthalic acid, dimethyl ester	Y	Y	Y	Y	Y
131179	Phthalic acid, diallyl ester	Y	N	N	Y	Y
542427	Palmitic acid, calcium salt	N	N	N	N	N
557051	Stearic acid, zinc salt	Y	N	N	N	N
683181	Dibutyltin dichloride	Y	N	Y	Y	Y
1241947	Phosphoric acid, 2-ethylhexyl diphenyl ester	Y	N	Y	Y	Y
1330785	Phosphoric acid, tritolyl ester	Y	N	Y	Y	Y
1330865	Adipic acid, diisooctyl ester	N	N	N	N	N
1333864	Carbon black	Y	Y	N	Y	N
1461229	Tributyltin chloride	Y	N	Y	Y	Y
1592230	Stearic acid, calcium salt	Y	N	N	Y	N
2528361	Phosphoric acid, dibutyl phenyl ester	Y	N	Y	Y	Y
6422862	Terephthalic acid, bis(2-ethylhexyl) ester	Y	Y	Y	Y	Y
6865356	Stearic acid, barium salt	Y	N	N	N	N
8002742	Paraffin waxes	Y	Y	N	N	N
8013078	Soybean oil, epoxidized	Y	N	Y	Y	Y
8016113	Linseed oil, epoxidized	N	N	N	N	N
8030782	Quaternary ammonium compounds	Y	N	N	Y	Y
16958922	Adipic acid, ditridecyl ester	N	N	N	N	N
26761400	Phthalic acid, diisodecyl ester	Y	Y	Y	Y	Y
27178161	Adipic acid, diisodecyl ester	Y	N	N	N	N
28553120	Phthalic acid, diisononyl ester	N	N	N	N	N
29761215	Phosphoric acid, isodecyl diphenyl ester	Y	N	Y	Y	Y
31566311	Glycerol monostearate	Y	N	N	N	Y
33703081	Adipic acid, diisononyl ester	N	N	N	N	N
56803373	Phosphoric acid, (1,1-dimethylethyl)phenyl diphenyl ester	Y	Y	Y	Y	Y

The above table shows that only a few additives were tested for these basic indicators of toxicity. Most other additives in use today are not tested.

The EINECS database had 100,106 entries in 1999, though in reality there are fewer chemicals actually on the market. Recent data from the European Commission's Joint Research Centre suggests that the numbers of substances in the different tonnage categories are as follows:

1-10 tons per annum (tpa) — 17,500 substances
10-100 tpa — 4,977 substances
100-1,000 tpa — 2,641 substances
>1,000 tpa — 2,704 substances

The category of over 1000 tpa is European equivalent of EPV chemicals in the USA. In this category, only 14% of the EU High Production Volume Chemicals had data publicly available at the level of the base set used for new chemicals marketed at one ton per annum or above, 65% had some data but less than base set, and 21% had no data.

The above shows how limited is health and safety information and a major effort is required to rectify this situation.

12.2 CARCINOGENIC EFFECT

To regulate carcinogenic substances, Federal agencies follow rulemaking procedures. Rulemaking procedures may be:

- risk-based (for example, the Delaney clause that bans a food additive shown to cause cancer in humans or in animal tests),
- technology-based, which might require the use of "best available technology" or "best practical technology" to control emissions from a particular source,
- risk-benefit or cost-benefit balancing, which permits the consideration of competing health risks and benefits (for example, cancer-causing drugs treat fatal illnesses but may affect other organs).[3]

The Occupational Safety and Health Act of 1970 established the Occupational Safety and Health Administration, OSHA, and the National Institute for Occupational Safety and Health, NIOSH. OSHA is a regulatory agency which, among its other duties, issues and enforces regulations that limit exposure to carcinogens in the workplace. NIOSH is a research agency that has supported epidemiological and toxicological research and makes recommendations to OSHA concerning changes in occupational health standards.[3]

In its rulemaking procedure, OSHA has used two different approaches for limiting exposures: setting permissible exposure limits and requiring specific process technology and procedures. In addition to the data from the National Toxicology Program, NTP, OSHA also considers the classification of the International Agency for Research on Cancer, IARC. Based on these data OSHA makes its own decisions. Table 12.2 contains information on substances used in PVC processing and included on the lists of carcinogens.

Table 12.2. Carcinogen lists

Chemical substance	IARC	NTP	OSHA-Z
Antimony trioxide	2B		
Cadmium and cadmium compounds	1	K	
Carbon black	2B		
Chlorinated paraffins (C12, 60% chlorine)	2B	P	
Di-(2-ethylhexyl) phthalate		P	
Lead and lead compounds	2B	P	Z
Silica, crystalline (respirable size)		K	
Talc containing asbestiform fibers	1		
Vinyl chloride	1	K	Z
Wood dust	1	K	

1 known human carcinogen
2A probable human carcinogen
2B possible human carcinogen
K known to be human carcinogen
P reasonably anticipated to be a human carcinogen
Z the chemical appears at 29 CFR part 1910 subpart Z

Table 12.2 shows that carcinogenic effect can be expected from monomer, plasticizers, stabilizers, and fillers. Some additives are only theoretically dangerous (e.g., chloroparaffins, crystalline silica, talc containing asbestiform fibers, and cadmium stabilizers) because they have been replaced in most countries some time ago. Other (lead compounds) are rapidly losing market share.

Published papers concentrate on the most important health issues, including:

- monomer present in manufacture,[4-9]
- monomer leached to water from water pipe,[10-13]
- dioxin formation during incineration,[14]
- plasticizers.[15-26]

In January 1974, the B.F. Goodrich site in Louisville, KY that produced vinyl chloride and polyvinyl chloride reported on the death of three workers diagnosed with angiosarcoma of the liver. This discovery was critical in linking industrial exposure and cancer.[10] It triggered an immediate reaction from OSHA, which reduced workplace exposure limit from 200 ppm to 1 ppm. Today, vinyl chloride is still considered carcinogenic but the danger was eliminated by manufacturing technology and process controls. There are studies being conducted to learn from this lesson and to assure that present standards are safe.[5-9] In one study, concentration of thioglycolic acid, a major metabolite of vinyl chloride, was conducted among workers in a PVC plant.[5] It was confirmed that thioglycolic acid assay is useful as an exposure marker but only for workers exposed to concentrations greater than 5 ppm.[5]

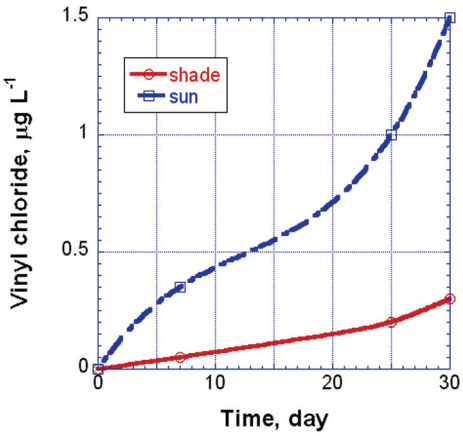

Figure 12.1. Concentration of vinyl chloride in water contained within exposed PVC pipe vs. exposure time. [Data from Al-Malack, M. H.; Sheikheldin, S. Y., *Water Res.*, **35**, 14, 3283-3290, 2001.]

In the studies of cancer incidents among PVC plant workers in a factory in Norway based on data from 1953 to 1993, excessive malignant melanoma (skin cancer) and spinocellular cancer were observed but no reason has been found nor it is certain that this is not a casual relationship, since no international large scale study was conducted.[6]

There is very little doubt that liver angiosarcoma is caused by lethal doses of vinyl chloride,[5,7,10] although it should be noted that the liver function assessment only including liver function tests is not able to detect vinyl chloride-induced liver damage, but reveals alterations due to non-occupational factors, such as dietary and/or metabolic dysfunctions.[8] There were also suggestions that brain cancer is caused by exposure to vinyl chloride but this was only supported by the data from Louisville, Kentucky but rejected based on data from other locations.[7] A new finding indicates that working longer than 3.5 years as a PVC bagger increases more than twofold the lung cancer risk.[9] It should be indicated that PVC dust is currently classified in group 3 by IARC and as a nuisance dust by ACGIH, therefore new experimental and epidemiological studies would be needed to examine these findings.

In the early 1990s, vinyl chloride monomer was found in a rural water system that included PVC pipe manufactured prior to 1977.[12] The amount of migrating vinyl chloride depends upon temperature and water residence time (long dead-end runs increase potential concentrations).[12] Water pipes produced prior to 1977 are at risk of vinyl chloride leaching above accepted limit of 2 µg L^{-1}.[10] More than 86% of pipe and fitting samples recently tested by NSF International were nondetectable for residual vinyl chloride at 0.1 ppm.[11] Vinyl chloride levels in U.S.-produced food packaging were 50% lower than the proposed standard of 10 ppb.[11]

In most cases, it is suggested that the older pipes are a problem because they had larger concentrations of vinyl chloride when they were produced.[10-12] This will stipulate higher concentration of vinyl chloride in PVC polymer but after 1974 it was not likely since vinyl chloride emissions were already limited by regulations. Thermal degradation is not known to produce vinyl chloride at the early stages of degradation. Apparently, this is not a case of UV exposure which produces measurable quantities of vinyl chloride (Figure 12.1). In this study, sections of PVC pipe had both ends blocked. Pipes were filled with water and exposed to the outdoor conditions in Saudi Arabia.[13] The amount of UV energy affects the rate of vinyl chloride release and migration.

Incineration of PVC wastes was found to cause emissions of heavy metals (from stabilizers) and dioxins (polychlorinated dibenzo-p-dioxins).[14] In addition to their high cancer risks, dioxins adversely affect the immune and endocrine systems and the development of foetuses.[14] Dioxin emission can be suppressed if the combustion temperature is controlled above 800°C. It was found that addition of $CaCO_3$ can also significantly suppress formation of dioxins both in gas and ash.[14] The dioxins trapped in ash will not affect environment because they are expected to be decomposed in the presence of titanium dioxide which was also added.[14]

It was found that dibutyl phthalate and diisononyl phthalate cause liver cancer in rats and have an adverse effect on the reproductive development of young rats.[15] This and other similar findings contributed to a large number of studies which later influenced the use of phthalate plasticizers in PVC. Since phthalate plasticizers are very effective in PVC plasticization it has caused many difficulties and setbacks for PVC industry.[16-25]

Later it was found that the chronic cancer and noncancer effects of DINP on rodent liver are consistent with its known action as a peroxisome proliferator.[16] Peroxisome proliferation is a threshold-based effect that is reversible on cessation of exposure to proliferators such as DINP.[16] Because rodents are uniquely responsive and humans and nonhuman primates are particularly nonresponsive to peroxisome proliferators, rodents are very poor animal models for use in human risk assessment of adverse effects mediated through peroxisome proliferation.[16]

One direction of studies was related to use of plasticizers in children's toys.[16,17,18,25,26] In the study of DINP it was concluded that soft PVC toys and other children's products do not present a significant risk to children.[16] The scientific evidence supports the continued use of DINP as a plasticizer in children's products.[16,25] In the case of di-2-ethylhexyl phthalate, DOP, it was found that its migration and intake can be sufficiently reduced if part of DOP is replaced by a permanent plasticizer such as blending with NBR.[17]

In Germany, daily intake of DOP (or DEHP) was studied based on urinary levels of its metabolites such as mono-(2-ethyl-5-hydroxyhexyl)phthalate, mono-(2-ethyl-5-oxohexyl)phthalate, and mono-(2-ethylhexyl)phthalate.[18] DOP is suspected to be an endocrine disrupting/modulating substance in humans, and children are of special concern due to their developmental state.[18] It was found that the majority of children are exposed to quantities below tolerable daily intake but younger children seem to be more severely burdened, most likely due to a higher food consumption, mouthing behavior, and/or playing near the ground.[18]

In Japan, human volunteers chewed PVC products under controlled conditions for 60 min. and then the amount of DINP migrated to saliva was determined by HPLC.[26] It was concluded (similar to the above studies) that children's toys containing DINP are safe for use for children.[26]

The other potential effects of plasticizers were studied in food packaged in PVC products,[19] indoor dust,[20] and especially exposure of patients to medical tubing.[21-24] Although it is acknowledged that migrating plasticizers should be replaced by more per-

manent additives, there is no evidence so far reported of harmful effects which will call for immediate withdrawal of these kinds of products.

12.3 TERATOGENIC AND MUTAGENIC EFFECT

Toxic effects are often studied in a "life stage specific" manner. Developmental toxicity is addressed by exposing pregnant mothers and looking for adverse effects in fetuses. Developmental toxicity is detected as death, structural malformations, or reduced weights of the fetuses just prior to birth. Reproductive toxicity is studied by exposing sexually mature adults to the chemical of interest. The effects of exposure are detected as impaired capacity to reproduce. Toxicologists realize now that exposure during one part of the life cycle could lead to adverse effects that might only be apparent at a different part of the life cycle.[27]

There are several important definitions which are used in the studies of the reproductive cycle, as follows:

Table 12.3. Definitions

Term	Definition
teratogen	an agent that increases the incidence of a congenital malformation
endocrine disrupter	an exogenous agent which interferes with synthesis, secretation, transport, binding, action, or elimination of natural hormones in the body which are responsible for the maintenance or homeostasis, reproduction, development, or behavior
mutagen	a substance capable of inducing or accelerating changes in a gene or chromosome

Various sources provide conflicting information on teratogenic and mutagenic properties of PVC additives (especially plasticizers).[28-30] In an earlier publication,[28] numerous plasticizers are shown to have teratogenic properties, but most recent data[29] and regulations[30] do not show that plasticizers are suspected teratogens or mutagens. The Gene-Tex database lists only di-(2-ethylhexyl) phthalate and di-(2-ethylhexyl) adipate as mutagens. It shows that studies on mutagenicity of dibutyl phthalate are inconclusive. It is very difficult to draw conclusions regarding these properties of plasticizers.

At the same time, the National Toxicology Program, NTP, established the NTP Center for the Evaluation of Risks to Human Reproduction, CERHR, in 1998. CERHR broadly solicits nominations of chemicals for evaluation from the public and private sectors. The CERHR convenes a scientific Expert Panel that meets in a public forum to review, discuss, and evaluate the scientific literature on the selected chemicals. In 1999, the CERHR recommended seven phthalates for expert panel review, including di-(2-ethylhexyl) phthalate, diisononyl phthalate, diisodecyl phthalate, di-n-butyl phthalate, butyl benzyl phthalate, di-n-octyl phthalate, and di-n-hexyl phthalate.

Some reports of expert panels were already released.[27,31-35] Table 12.4 gives a summary of conclusions.

Table 12.4. Effect of some phthalates on developmental and reproductive toxicities[27,31-35]

Plasticizer	Developmental toxicity	Reproductive toxicity	
		Male	Female
benzyl butyl phthalate	clear evidence minimal concern	some evidence negligible concern	limited evidence insufficient hazard
diisononyl phthalate	some evidence/minimal concern	limited evidence/minimal concern	
di-n-butyl phthalate	clear evidence/minimal concern	clear evidence/negligible concern	
diisodecyl phthalate	clear evidence/minimal concern	some evidence/negligible concern	
di-n-hexyl phthalate	clear evidence/minimal concern	some evidence/negligible concern	
di-n-octyl phthalate	limited evidence/insufficient hazard	some evidence/negligible concern	

It is noticeable that in all cases the expert panel considered risks of developmental and reproductive toxicities as minimal or negligible. This is because the levels of exposure are much smaller than the levels considered sufficient to cause the effect.[27,31-35]

Some plasticizers, including di-(2-ethylhexyl) phthalate, butyl benzyl phthalate, di-n-butyl phthalate, dicyclohexyl phthalate, diethyl phthalate, di-(2-ethylhexyl) adipate, dipentyl phthalate, dihexyl phthalate, dipropyl phthalate, are on the lists of substances having endocrine disrupting effects.[36] Endocrine disrupting compounds are of great concern because they are active at very low concentrations. On the other hand, sufficient studies do not exist yet to establish concentrations which may be needed for such an effect to occur.[37] There is no consistent method selected which may quantify this effect.[37,38]

The following conclusion were included regarding the effect of DOP (DEHP):[39]

- The NTP concurs with the CERHR DEHP Update Expert Panel that for pregnant women not medically exposed to DEHP, available toxicity data and estimates of human exposure to DEHP lead to a conclusion of some concern for adverse effects on male offspring.
- The NTP concurs with the CERHR DEHP Update Expert Panel that there is minimal concern for reproductive toxicity in exposed adults. This level of concern is not altered for adults medically exposed to DEHP or MEHP.

The above statements are in agreement with published results of studies in open literature.[4,22,40]

Some organotin compounds are known to be teratogenic *in vivo*. These include di-n-butyltin dichloride and bis(tri-n-butyltin)oxide, TBTO.[41] The teratogenicity of TBTO in mice indicates that malformation occurred at dosages moderately toxic to the mother. Di-n-octyltin dichloride has been reported to be immunosuppressive in rats.[41]

The thermal decomposition of PVC plastics is known to generate mutagenic polycyclic aromatic hydrocarbons, e.g., phenanthrene, pyrene, benzo[a]pyrene, and benzo[e]pyrene.[42]

12.4 ALLERGY

Contact allergy to polyvinylchloride (PVC) gloves has been reported.[43] Two patients reacted to a technical PVC antioxidant and one to triphenyl phosphite.[43] Contact allergy to triphenyl phosphite was very strong and was the main cause of her hand dermatitis.[43] Three other patients reacted to PVC gloves, but the specific allergen was not identified.[43]

12.5 WORKPLACE EXPOSURE LIMITS

There are numerous limiting values set to protect employees against workplace exposures. The definitions of these values are given below:

Threshold Limit Value, TLV, is an exposure standard set by a committee of the American Conference of Governmental Industrial Hygienists, ACGIH. The TLVs are published annually. The guidelines are based on available animal and human exposure studies. The rationale for setting the TLVs is given in an ACGIH publication.[44] The ACGIH committee is independent and flexible, incorporates new data rapidly, and is relatively free of bureaucratic constraints of official government agencies. The TLV's are recommended values, not legal limits. They do not guarantee protection to all workers and they are not intended to be used for community exposure. TLVs are values that should not be exceeded. The goal is to minimize workers' exposure to hazardous concentrations as much as possible.[45]

Recommended Exposure Limits, REL, are set by the National Institute for Occupational Safety and Health, NIOSH, which is a part of the department of Health and Human Services. NIOSH scientists recommend exposure limits to OSHA, based on animal and human studies. NIOSH RELs are often more conservative than the TLV, and NIOSH's consideration of available research and studies is regarded as thorough.[45]

Permissible Exposure Limits, PEL, are set by the Occupational Safety and Health Administration, OSHA, and are the law of the land in the United States. Workers' exposure may not exceed these standards and OSHA has the power to warn, cite, and fine violators. The Act required OSHA to set standards that will provide safe working conditions by negotiation and consensus. As a result, only about 25 permanent standards have been set since 1973. To protect workers in the meantime, OSHA was allowed to adopt existing standards or develop Emergency Temporary Standards (ETS). OSHA adopted the ACGIH TLV as the interim standard, giving legal status to what was meant to serve as recommended limits. The permanent standards are thorough and reflect the extensive effort invested in their preparation. They include action levels that are typically half the TWA exposure limits. When the action limit is exceeded, several steps must be taken such as medical monitoring, air sampling, and control measures. Each permanent standard includes recommendations for air sampling procedures, regulations for record keeping, engineering control methods, labeling and warning, and other pertinent regulations.[45] The PELs are published in 29 CFR 1910.1000.[46]

Time-Weighted Average, TWA, is the concentration of contaminants over an 8-hour period. It is determined by sampling the breathing zone of the worker for 8 hours. It is expressed as follows when a series of successive samples have been taken:

$$TWA = \sum_i C_i t_i / \sum t_i \qquad [12.1]$$

where:

t_i the period of time during which one sample is taken
C_i the average concentration over time period t_i.

To determine the level of exposure, the TWA reading is compared with a standard such as the threshold limit value, TLV, or permissible exposure limit, PEL. If the reading exceeded the standard, overexposure occurred.[45]

Short-Term Exposure Limit, STEL, is a 15-minute TWA concentration that may not be exceeded, even if the 8-hour TWA is within the standards. TWA-STEL are given for contaminants for which short-term hazards are known. For the rest, an excursion factor of 3 has been often used: STEL should not exceed 3 times the TWA limit.[45]

Ceiling is a concentration that should not be exceeded at any time. Note that both TWA and STEL permit limited excursion if, in the end, the average is below the exposure limit. The ceiling value, however, may not be exceeded.[45]

Immediately Dangerous to Life and Health, IDLH, is defined as conditions that pose immediate danger to life or health, or conditions that pose a threat of severe exposure. IDLH limits are created mainly to assist in making decisions regarding respirator use: above the IDLH only supplied air respirators should be used, below the IDLH, air purifying respirators may be used, if appropriate. Two factors were considered when establishing the IDLH limits:

- workers must be able to escape such an environment without suffering permanent health damage
- workers must be able to escape without severe eye or respiratory tract irritation or other conditions that might impair their escape

The current definition has no exposure duration associated with it. Workers should not be in an IDLH environment for any length of time unless they are equipped and protected to be in that environment. IDLH values were determined based on animal and human data. They may be found in the NIOSH Pocket Guide to Chemical Hazards.[47]

Occupational Exposure Limits, OELs, are set by the European Union. In 1990, at the request of the Council, the European Commission had set up an informal group of scientists, known as the Scientific Expert Group, SEG, to give advice on setting limit values, after having reviewed the different approaches in the Member States. To encourage the Occupational Exposure Limits, OELs, the European Commission decided to formalize the SEG and with its Decision 95/320/EC of 12 July 1995 has set up a formal base for the work on the scientific evaluation of risk at the workplace related to chemical substances.[48] The proposed values include:

- the eight-hour time weighted average, TWA
- short-term/excursion limits, STEL

Table 12.5 gives limits for air contaminants for additives available from OSHA[46] and NIOSH.[47]

Table 12.5. Limits for air contaminants from OSHA[46] and NIOSH[47]

Plasticizer	PEL, mg m^{-3}	REL, mg m^{-3}	IDLH, mg m^{-3}
Antimony trihydrate	0.5	0.5	25.5
Arsenic organic compounds (as As)	0.5	-	-
Barium sulfate (respirable fraction)	5	5	
Cadmium and cadmium compounds (as Cd)	0.005	0.005	9
Calcium carbonate (respirable fraction)	5	5	-
Carbon black	3.5	3.5	1750
Dibutyl phosphate	5	5	258
Dibutyl phthalate	5	5	4000
Diethyl phthalate	-	5	-
Dimethyl phthalate	5	5	2000
Di-(2-ethylhexyl) phthalate	5	5	5000
Hydrogen chloride	7	7	74.5
Lead and lead compounds (as Pb)	0.05	0.05	100
Particulates (not otherwise regulated) (respirable fraction)	5	-	-
Tin organic compounds (as Sn)	0.1	0.1	25
Titanium dioxide (total dust)	15	-	5000
Tributyl phosphate	5	2.5	326.7
Tri-o-cresyl phosphate	0.1	0.1	40
Triphenyl phosphate	3	3	1000
Vinyl chloride	1 (ppm)	-	-
Zinc stearate (respirable fraction)	5	5	-

12.6 EXPOSURE FROM CONSUMER PRODUCTS

Superfund Amendments and Reauthorization Act, SARA requires that the Agency for Toxic Substances and Disease Registry, ATSDR, develops jointly with the U.S. Environmental Protection Agency, EPA, a list of hazardous substances most commonly found at facilities, prepare toxicological profiles for each substance included on the priority list of hazardous substances, and ascertain significant human exposure levels, SHELs, for hazardous substances in the environment, and the associated acute, subacute, and chronic health effects. The ATSDR Minimal Risk Levels, MRLs, were developed as an initial response to the mandate. An MRL is an estimate of the daily human exposure to a hazardous substance that is likely to be without appreciable risk of adverse noncancer health effects over a specified duration of exposure.[49]

MRLs are based on noncancer health effects only. Oral MRLs are expressed as daily human doses in units of milligrams per kilogram per day (mg kg^{-1} day^{-1}). ATSDR uses the no-observable-adverse-effect-level/uncertainty factor, NOAEL/UF, approach to derive MRLs for hazardous substances. There are set below levels that, based on current information, might cause adverse health effects in the people most sensitive to such substance-induced effects. MRLs are derived for acute (1-14 days), intermediate (>14-364 days), and chronic (365 days and longer) exposure durations.[49]

Table 12.6 gives Minimal Risk Levels for additives.

Table 12.6. Minimal Risk Levels available for additives and admixtures[49] (oral doses)

Additive	Acute, mg kg^{-1} day^{-1}	Chronic, mg kg^{-1} day^{-1}
Cadmium		0.0002
Di-(2-ethylhexyl) phthalate	0.1	0.06
Di-n-butyl phthalate	0.5	-
Di-n-octyl phthalate	3	0.4*
Diethyl phthalate	7	6*
Tin, dibutyl		0.005*
Tin, tributyl		0.0003
Vinyl chloride		0.003
Zinc		0.3

*intermediate

Individual exposure depends on a cumulative action from various sources such as workplace exposure, amounts of substance contained in water, air, indoor environment (as a consequence of use of various products by construction and maintenance), food products, food packaging, household products, and cosmetics. The total exposure should not exceed the above values.

A publication[50] gives data on the contents of plasticizers in cosmetics such as deodorants, perfumes, hair mousses, hair gels, and hair sprays manufactured by leading European producers. The following phthalates were found in European cosmetics: butyl benzyl, di-n-butyl, di-(2-ethylhexyl), diethyl, dimethyl, and di-n-octyl phthalate. Diethyl phthalate is the most frequently used. The following ranges of concentrations of diethyl phthalate were determined in various groups of products:[50]

deodorants	40 to 1,600 mg/kg
perfumes	210 to 19,000 mg/kg
hair mouses	8 to 1,700 mg/kg
hair sprays	92 to 5,700 mg/kg

In order to reach a Minimal Risk Level for diethyl phthalate from Table 12.6, a 60 kg person needs to use only 20 g of some of these products. If one compares these very high concentrations of plasticizers with relatively low limits for air contaminants (Table 12.4) it becomes pertinent that sometimes workers are better protected from toxic chemicals than

are the users of cosmetic products (frequently very expensive designer cosmetics). The problem is aggravated by the lack of regulations which may force manufacturers to reveal the composition of their products. Frequently, information on a product label lists only a few natural raw materials but completely omits all of the many synthetic materials used in formulation. In view of increasing dangers to the public, regulatory actions should take place to require manufacturers to fully disclose harmful components of their products. It will also be useful to require some justification as to why such materials must be added to the formulation.

12.7 DRINKING WATER

Drinking water protection is based on the Safe Drinking Water Act, which authorizes the EPA to develop regulations, to set nationwide uniform drinking water quality standards for all states, and to implement programs to ensure the safety of public water supplies and to protect public health. State and local environmental agencies ensure that public water systems test drinking water regularly to ensure its safety. Drinking water testing includes bacteria, nitrates, inorganic and organic chemicals, radioactive elements, lead, and copper. The exact number of contaminants a system must test for is determined by the extent to which they are present in the source of the water. The 1986 Amendments to the Safe Drinking Water Act, SDWA, authorize USEPA to set maximum levels of contaminants allowable in drinking water.

Two plasticizers: di-(2-ethylhexyl) phthalate[51] and di-(2-ethylhexyl) adipate[52] were included by EPA in a group of Specified Organic Chemical, presence of which is tested by local authorities. Maximum Contaminant Level, MCL, established by EPA is 6 μg/l for di-(2-ethylhexyl) phthalate, DOP, and 400 μg/l for di-(2-ethylhexyl) adipate. Various states followed with their own regulations and MCLs listed in Table 12.7.

Table 12.7. Water testing criteria in various states. Di-(2-ethylhexyl) phthalate[53]

State	Description	MCL, μg/l	Reference
Alaska	MCL	6	AK Dept. Environ. Conservation 1999
Arizona	Aquifer water quality standard	6	BNA 2001
California	MCL	4	CA Dept. of Health Services 2000
Colorado	Ground water organic chemical standard	6	CO Dept. of Public Health & Env. 1999
Kentucky	Maximum allowable instream concentration	1.8	BNA 2001
Maine	Drinking water guideline	25	HSDB 2001
New Jersey	Groundwater quality criteria	3	NJ Dept. of Env. Protection 1993
Rhode Island	Ground water quality standard	6	BNA 2001
South Dakota	MCL	6	SD Dept. of Env. & Natural Resources 1998
Vermont	Enforcement standard	6	BNA 2001

Table 12.7 shows that states have, in most instances, similar or more stringent levels of plasticizers compared with federal values established by EPA. In New York City samples of water are tested for plasticizer concentration from 4 to 45 samples per year depending on the system. The most frequently tested are ground water system samples (45 samples/year). In 1998, only one sample contained 0.6 μg/l of DOP (10 times below the Maximum Contaminant Level). In other samples plasticizers were not detected.[54] Data[55,56] show that some amounts of plasticizers are detected in drinking water plants, groundwater sources, and rivers worldwide, but these are usually in parts per billion concentrations well below the Maximum Contaminant Level established by the EPA.[51,52]

On the other hand, the EPA Toxic Release Inventory shows that large quantities of plasticizers were released in water and land in the period from 1987 to 1993 (di-(2-ethylhexyl) phthalate: water 16,910 lbs, land 471,191 lbs; di-(2-ethylhexyl) adipate: water 27,471, land 425,230 lbs).[51,52]

There are two main reasons why plasticizer release in to the environment does not increase its concentration in a water system. Di-(2-ethylhexyl) adipate and phthalate are absorbed on soil and they do not leach into water when released to land. They are also biodegradable (di-(2-ethylhexyl) adipate: 2.7 days of a half-life, di-(2-ethylhexyl) phthalate: 2-3 weeks of a half-life). Atmospheric bound vapors and mists will travel long distances and will be ultimately deposited on land with rain water.[51,52]

Contamination of water by vinyl chloride was discussed in Section 12.2.

12.8 FOOD REGULATORY ACTS

In the United States, the Food and Drug Administration is entrusted by a Code of Federal Regulations[57] to control use of different materials in production of food and its packaging. Two types of additives are used in connection with food: additives permitted to be added to food directly and additives which are used in materials in contact with food products.

Table 12.8 shows the relevant parts of Regulation[57] and additives which may be directly added to food.

Table 12.8. PVC additives can be added directly to food[57]

Part	Plasticizer
Part 172. Food Additives Permitted for Direct Addition to Food for Human Consumption	
172.180	Stannous chloride (asparagus only)
172.480	Silicon dioxide
172.723	Epoxidized soybean oil
172.804	Azodicarbonamide
172.860	Fatty acids (including lauric acid, myristic acid, oleic acid, palmitic acid, and stearic acid)
172.866	Synthetic glycerin produced by the hydrogenolysis of carbohydrates
Part 182--Substances generally recognized as safe	
182.1057	Hydrochloric acid
182.8985	Zinc chloride
182.8994	Zinc stearate

Table 12.8. PVC additives can be added directly to food[57]

Part	Plasticizer
Part 184 - Direct food substances affirmed as generally recognized as safe	
184.1191	Calcium carbonate
184.1193	Calcium chloride
184.1229	Calcium stearate
184.1323	Glyceryl monooleate
184.1324	Glyceryl monostearate
184.1409	Ground limestone
184.1901	Triacetin
184.1911	Triethyl citrate

Table 12.9 shows the relevant parts of the Regulation[57] and components of PVC formulation sanctioned as indirect food additives.

Table 12.9. PVC formulation components permitted as indirect additives to food[57]

Part	Description	Plasticizers
Part 175 - Indirect food additives: Adhesives and components of coatings		
175.105	Adhesives	acetyl tributyl citrate, acetyl triethyl citrate, antimony oxide, barium sulfate, butyl benzyl phthalate, butyldecyl phthalate, butyloctyl phthalate, carbon black (channel process), chlorinated liquid n-paraffins with chain lengths of C10-C17, containing 40-70 percent chlorine by weight, cresyl diphenyl phosphate, di-(butoxyethyl) phthalate, di-(C7,C9-alkyl) adipate, dibutyl phthalate, dibutyl sebacate, dicyclohexyl phthalate, diethylene glycol adipic acid copolymer, diethylene glycol dibenzoate, diethylene glycol copolymer of adipic acid and phthalic anhydride, di-(2-ethylhexyl) adipate, di-(2-ethylhexyl) hexahydrophthalate, di-(2-ethylhexyl) phthalate, diethyl phthalate, dihexyl phthalate, diisobutyl adipate, diisobutyl phthalate, diisodecyl adipate, diisodecyl phthalate, diisooctyl phthalate, dimethyl phthalate, di-n-octyldecyl adipate, dioctylphthalate, dioctylsebacate, diphenyl 2-ethylhexyl phosphate, diphenyl phthalate, dipropylene glycol dibenzoate, dipropylene glycol copolymer of adipic acid and phthalic anhydride, fatty acid salts of calcium and zinc, octyldecyl phthalate, polyethylene glycol (molecular weight 200-6,000), polymeric esters of polyhydric alcohols and polycarboxylic acids, polypropylene glycol dibenzoate levels not to exceed 20 wt%, soybean oil epoxidized, stearamide, titanium dioxide, tributoxyethyl phosphate, tributylcitrate, tributyl phosphate, triethylene glycol dibenzoate, triethylhexyl phosphate, triethylphosphate, triphenylphosphate, tri-(p-tertiary butyl phenyl) phosphate
175.125	Pressure-sensitive adhesives	substances generally recognized as safe in food (see Table 12.8)
175.300	Resinous and polymeric coatings	glycerol, acetyl tributyl citrate, acetyl triethyl citrate, butyl phthalyl butyl glycolate, butyl stearate, p-tert-butyl phenyl salicylate, dibutyl sebacate, diethyl phthalate, diisobutyl adipate, diisodecyl phthalate (for use only as plasticizer in side seam cements for containers), diisooctyl phthalate, epoxidized soybean oil (iodine number maximum 14; oxirane oxygen content 6% minimum), as the basic polymer, ethyl phthalyl ethyl glycolate, 2-ethylhexyl diphenyl phosphate, di-(2-ethylhexyl) phthalate, glycerol, glyceryl monooleate, glyceryl monostearate, glyceryl triacetate, monoisopropyl citrate, polyvinyl chloride, propylene glycol, sorbitol, mono-, di-, and tristearyl citrate, triethyl citrate, triethylene glycol, 3-(2-xenolyl)-1,2-epoxypropane
175.320	Resinous and polymeric coatings for polyolefin films	acetyl tributyl citrate, acetyl triethyl citrate, butyl phthalyl butyl glycolate, butyl stearate, dibutyl sebacate, diethyl phthalate, 2-ethylhexyl diphenyl phosphate, ethyl phthalyl ethyl glycolate, glycerol monooleate, glycerol triacetate, polyvinyl chloride, triethyl citrate
175.380	Xylene-formaldehyde resins condensed with 4,4`-isopropylidenediphenol-epichlorohydrin epoxy resins	substances identified in Sec. 175.300

Table 12.9. PVC formulation components permitted as indirect additives to food[57]

Part	Description	Plasticizers
175.390	Zinc-silicon dioxide matrix coatings	substances for which safe conditions of use have been prescribed in Sec. 175.300
Part 176. Indirect Food Additives: Paper and Paperboard Components		
176.170	Components of paper and paperboard in contact with aqueous and fatty foods	dibutyl phthalate, dibutyl sebacate, di-(C7,C9-alkyl) adipate, dicyclohexyl phthalate, diethylene glycol dibenzoate (at a level not to exceed 5 wt%), dipropylene glycol dibenzoate, fatty acids salts of calcium and zinc
176.180	Components of paper and paperboard in contact with dry food	diethylene glycol dibenzoate, dipropylene glycol dibenzoate, polyvinyl chloride, and substances that by Sec. 176.170 and other applicable regulations in parts 170 through 189 of this chapter may be safely used as components of the uncoated or coated food-contact surface of paper and paperboard, subject to the provisions of such a regulation
176.210	Defoaming agents used in the manufacture of paper and paperboard	di-(2-ethylhexyl) phthalate, tributoxyethyl phosphate, tributyl phosphate, tri-(2-ethylhexyl) phosphate
176.300	Slimicides	dibutyl phthalate, didecyl phthalate, dodecyl phthalate in adjuvant substances
Part 177 - Indirect food additives: Polymers		
177.1010	Acrylic and modified acrylic plastics, semi-rigid and rigid	di-(2-ethylhexyl) phthalate, for use only as a flow promoter at a level not to exceed 3 wt% based on the monomers and dimethyl phthalate
177.1200	Cellophane	dibutyl phthalate, dicyclohexyl phthalate, dimethylcyclohexyl phthalate, diisobutyl phthalate, and di-(2-ethylhexyl) phthalate (alone or in combination with other phthalates where total phthalates do not exceed 5 percent), di-(2-ethylhexyl) adipate
177.1210	Closures with sealing gaskets for food containers	azodicarbonamide, calcium zinc stearate, di-(C7, C9-alkyl) adipate (complying with Sec. 178.3740 of this chapter; except that, there is no limitation on polymer thickness), di-2-ethylhexyl adipate, di-2-ethylhexyl sebacate (2%), di-2-ethylhexyl terephthalate (at levels not exceeding 75 parts per hundred by weight of permitted vinyl chloride homo- and/or copolymer resins used in contact with food of Types I, II, IV-B, VI-A, VI-B, VI-C (up to 15 percent alcohol by volume), VII-B, and VIII), diisodecyl phthalate (no limitation on amount used but for use only in closure-sealing gasket compositions used in contact with non-fatty foods containing no more than 8 percent of alcohol), epoxidized linseed oil, epoxidized safflower oil, epoxidized soybean oil, polyisobutylene
177.1400	Hydroxyethyl cellulose film, water-insoluble	Substances identified in and used in compliance with Sec. 177.1200
177.1460	Melamine-formaldehyde resins in molded articles	dioctyl phthalate (for use as lubricant)
177.2420	Polyester resins, cross-linked	butyl benzyl phthalate (containing not more than 1.0 wt% of dibenzyl phthalate), dibutyl phthalate, dimethyl phthalate, triphenyl phosphate

Table 12.9. PVC formulation components permitted as indirect additives to food[57]

Part	Description	Plasticizers
177.2600	Rubber articles intended for repeated use	Plasticizers (total not to exceed 30 wt% of rubber product unless otherwise specified): n-amyl n-decyl phthalate, butylacetyl ricinoleate, n-butyl ester of tall oil fatty acids, butyl laurate, butyl oleate, butyl stearate, calcium stearate, castor oil, coumarone-indene resins, 2,2`-dibenzamidodiphenyl disulfide, dibenzyl adipate, dibutoxyethoxyethyl adipate, dibutyl phthalate, dibutyl sebacate, didecyl adipate, didecyl phthalate, diisodecyl adipate, diisodecyl phthalate, diisooctyl adipate, diisooctyl sebacate, dioctyl adipate, dioctyl phthalate, dioctyl sebacate, dipentene resin, diphenyl ketone, fatty acids, fatty acids hydrogenated, isooctyl ester of tall oil fatty acids, lanolin, a-methylstyrene-vinyltoluene copolymer resins (molar ratio 1 α-methylstyrene to 3 vinyltoluene), mineral oil (in rubber articles complying with this section, not to exceed 30 wt%, alone or in combination with waxes, petroleum, total not to exceed 45 wt% of rubber articles that contain at least 20 wt% of ethylene-propylene copolymer elastomer complying with paragraph (c)(4)(i) of this section, in contact with foods of Types I, II, III, IV, VI, VII, VIII, and IX), montan wax., n-octyl n-decyl adipate, n-octyl n-decyl phthalate, petrolatum, petroleum hydrocarbon resin (cyclopentadiene type) hydrogenated, petroleum hydrocarbon resin (produced by the homo- and copolymerization of dienes and olefins of the aliphatic, alicyclic, and monobenzenoid arylalkene types from distillates of cracked petroleum stocks), petroleum hydrocarbon resin (produced by the catalytic polymerization and subsequent hydrogenation of styrene, vinyltoluene, and indene types from distillates of cracked petroleum stocks), petroleum oil, sulfonated, phenol-formaldehyde resin, pine tar, polybutene, polystyrene, propylene glycol, n-propyl ester of tall oil fatty acids, rapeseed oil vulcanized with rubber maker`s sulfur, rosins and rosin derivatives identified in sec. 175.105(c)(5) of this chapter, soybean oil vulcanized with rubber maker`s sulfur, styrene-acrylonitrile copolymer, terpene resins, triethylene glycol dicaprate, triethylene glycol dicaprylate, waxes, petroleum, xylene (or toluene) alkylated with dicyclopentadiene, zinc 2-benzamidothiophenate
Part 178. Indirect Food Additives: Adjuvants, Production Aids, and Sanitizers		
178.2010	Antioxidant and/or stabilizers for polymers	calcium stearate, dimethyltin/monomethyltin isooctylmercaptoacetates, di(n -octyl)tin bis(2-ethylhexyl maleate), ethylene bis(oxyethylene)-bis-(3- tert -butyl-4-hydroxy-5-methylhydrocinnamate), 2(2'-hydroxy-5'-methylphenyl)benzotriazole, 4,4'-isopropylidenediphenol alkyl(C12-C15) phosphites, poly[(1,3-dibutyldistannthianediylidene)-1,3-dithio], zinc stearate
178.2650	Organotin stabilizers in vinyl chloride plastics	di(n-octyl)tin S,S'-bis(isooctylmercaptoacetate), di(n-octyl) tin maleate polymer, C10-16-alkyl mercaptoacetates reaction products with dichlorodioctylstannane and trichlorooctylstannane, (n-octyl)tin S,S'S''tris(isooctyl-mercaptoacetate), bis(β-carbobutoxyethyl)tin bis(isooctylmercaptoacetate), β-carbobutoxyethyltin tris(isooctylmercaptoacetate), dodecyltin stabilizer
178.3280	Castor oil, hydrogenated	
178.3500	Glycerin, synthetic	
178.3740	Plasticizers in polymeric substances	the following plasticizers can be used with a number of limitations which can be found in the original Regulation:[33] butyl benzyl phthalate, 3-butylene glycoladipic acid polyester (1,700-2,200 molecular weight) terminated with a 16 percent by weight mixture of myristic, palmitic, and stearic acids, di-(C7, C9-alkyl) adipate, in which the C7, C9-alkyl groups are derived from linear α-olefins by the oxo process, di-n-alkyl adipate made from C6-C8-C10 (predominately C8 and C10) or C8-C10 synthetic fatty alcohols complying with Sec. 172.864, dicyclohexyl phthalate, di-(2-ethylhexyl) adipate, diisononyl adipate, diisononyl phthalate, di-(2-ethylhexyl) azelate, di-n-hexylazelate, dihexyl phthalate, diphenyl phthalate, epoxidized butyl esters of linseed oil fatty acids, epoxidized linseed oil, polybutene hydrogenated, polyisobutylene (mol weight 300-5,000), polyisobutylene complying with Sec. 177.1420, polypropylene glycol (CAS registry No. 25322-69-4) (minimum mean molecular weight 1,200), propylene glycol azelate (average mol. weight 3,000), triethylene glycol, 2,2,4-trimethyl-1,3-pentanediol diisobutyrate
178.3790	Polymer modifiers in semirigid and rigid vinyl chloride plastics	acrylic polymers and their copolymers
178.3910	Surface lubricants used in the manufacture of metallic articles	acetyl tributyl citrate, acetyl triethyl citrate, butyl stearate, castor oil, dibutyl sebacate, di-(2-ethylhexyl) azelate, di-(2-ethylhexyl) sebacate, diisodecyl phthalate, di-(2-ethylhexyl) phthalate, diethyl phthalate, di-n-octyl sebacate, epoxidized soybean oil, polyisobutylene (minimum molecular weight 300),

A European Union Directive contains references to some materials which may play a role of PVC additives in Annex I and Annex 2.[58] Table 12.10 gives a list of these materials.

Table 12.10. List of PVC additives included in EU Directives[58]

Section	Reference #	Name
Annex 1	18100	Glycerol
	23230	Phthalic acid, diallyl ester
	24550	Stearic acid
	24970	Terephthalic acid, dimethyl ester
	35760	Antimony trioxide
	36640	Azodicarbonamide
	41520	Calcium chloride
	47600	Di-n-dodecyltin bis(isooctyl mercaptoacetate)
	49595	Dimethyltin bis(ethylhexyl mercaptoacetate)
	49600	Dimethyltin bis(isooctyl mercaptoacetate)
	50160	Di-n-octyltin bis(n-alkyl(C10-C16) mercaptoacetate)
	50240	Di-n-octyltin bis(2-ethylhexyl maleate)
	50320	Di-n-octyltin bis(2-ethylhexyl mercaptoacetate)
	50360	Di-n-octyltin bis(ethyl maleate)
	50400	Di-n-octyltin bis(isooctyl maleate)
	50480	Di-n-octyltin bis(isooctyl mercaptoacetate)
	50560	Di-n-octyltin 1,4-butanediol bis(mercaptoacetate)
	50640	Di-n-octyltin dilaurate
	50720	Di-n-octyltin dimaleate
	50800	Di-n-octyltin dimaleate, esterified
	50880	Di-n-octyltin dimaleate, polymers
	50960	Di-n-octyltin ethyleneglycol bis(mercaptoacetate)
	51040	Di-n-octyltin mercaptoacetate
	51120	Di-n-octyltin thiobenzoate 2-ethylhexyl mercaptoacetate
	53360	N,N'-Ethylenebisoleamide
	53520	N,N'-Ethylenebisstearamide
	67360	Mono-n-dodecyltin tris(isooctyl mercaptoacetate)
	67515	Monomethyltin tris(ethylhexyl mercaptoacetate)
	67520	Monomethyltin tris(isooctyl mercaptoacetate)
	67600	Mono-n-octyltin tris(alkyl(C10-C16) mercaptoacetate)
	67680	Mono-n-octyltin tris(2-ethylhexyl mercaptoacetate)

Table 12.10. List of PVC additives included in EU Directives[58]

Section	Reference #	Name
Annex 1	67760	Mono-n-octyltin tris(isooctyl mercaptoacetate)
	74560	Phthalic acid, benzyl butyl ester
	74640	Phthalic acid, bis (2-ethylhexyl) ester
	74880	Phthalic acid, dibutyl ester
	75100	Phthalic acid, diesters with primary, saturated C8-C10 branched alcohols,
	75105	Phthalic acid, diesters with primary, saturated C9-C11 alcohols
	80000	Polyethylene wax
	86240	Silicon dioxide
	88640	Soybean oil, epoxidized
	88960	Stearamide
	89040	Stearic acid
	92080	Talc
	93760	Soybean oil, epoxidized
Annex 2	42080	Carbon black
	88640	Soybean oil, epoxidized

Further information on sanitary aspects of food packaging legislation can be found elsewhere.[59] This information includes PVC among other polymers.[59] Leachates from plastic consumer products were also screened for toxicity with *Daphnia magna*.[60] The following plasticized PVC articles displayed toxicity: artificial leather, bath tub toy, inflatable bathing ring and table cloth.[60]

12.8 TOXICITY OF STABILIZERS

Table 12.11 contains information on available LD50 values characterizing the toxicity of chemical materials. Lethal Dose 50, LD50, is the dose of a chemical which kills 50% of a sample population. In full reporting, the dose, treatment, and observation period should be given. Further, LD50, LC50, ED50 and similar figures are only comparable when the age, sex, and nutritional state of the animals is specified.

Table 12.11. LD50 of stabilizers and its products of reaction with HCl

Stabilizer group	LD50 oral rat, mg/kg	LD50 rabbit dermal, mg/kg	LD50 oral mouse, mg/kg
Ba/Ca/Zn carboxylates	not available		
Ba/Zn carboxylates	not available		
Ba stearate	2,506–3,390		1,832

Table 12.11. LD50 of stabilizers and its products of reaction with HCl

Stabilizer group	LD50 oral rat, mg/kg	LD50 rabbit dermal, mg/kg	LD50 oral mouse, mg/kg
$CaCl_2$	1,000		42
Ca/Zn carboxylates	not available		
Ca stearate	>10,000		>10,000
K/Zn carboxylates	not available		
Mg/Zn carboxylates	not available		
Zn carboxylates	>10,000		>10,000
$ZnCl_2$	2,000		329–1,250
Stearic acid	4,600		
Butyltin carboxylates	32–175	100-500	46-109
Butyltin mercaptides	330–2,300		
Butyltin mercaptides/carboxylates	not available		
Bu_2SnCl_2	100		35–70
Methyltin mercaptides	1100–1840		
Me_3SnCl	12,600		
Octyltin carboxylate	not available		
Octyltin mercaptide	not available		
Organotin mercaptide	>800–2,500		
Tributyltin	not available		
Tetrabutyltin		500	6,000
Dibutyltin oxide	44.9–180		
$BuSnCl_3$	2,140		1,400
$SnCl_4$	700		1,200
Lead stearate	>2,000		
Lead sulfate	not available		
Dibasic lead phosphite	not available		
Dibasic lead phthalate	>2,000		
Dibasic lead stearate	not available		
Dibasic lead sulfate	>2,000		
Tribasic lead maleate	not available		
Tribasic lead sulfate	>2,500		
Tetrabasic lead fumarate	not available		
Tetrabasic lead sulfate	not available		
Benzophenones	>2,000–>10,000		
Benzotriazoles	>2,000–>10,000		>6,500–>7,750

Table 12.11. LD50 of stabilizers and its products of reaction with HCl

Stabilizer group	LD50 oral rat, mg/kg	LD50 rabbit dermal, mg/kg	LD50 oral mouse, mg/kg
Cyanoacrylates			>5,000
HALS	>2,000–>7,750		
Oxalanilides	>2,000		
Phenolic antioxidants	>2,000–>10,000		
Phosphites	167–>10,000		>10,000

Two conclusions are pertinent:

- with the exception of some tin compounds, stabilizers have low toxicity (toxicity of cadmium compounds is excluded here)
- very little is known about the toxicity of the most popular stabilizers, some of which were in production and use for more than 50 years. These gaps are marked by "not available" in order to show that these data would have been included if they could be found in either open literature or MSDSs of their manufacturers.

Table 12.12 shows the effect of stabilizers on test organisms.

Table 12.12. Toxicity of stabilizers and its products of reaction with HCl to test organisms.

Stabilizer group	Fish, 96H, LC50, mg/kg	Daphnia magna, 48H, EC50, mg/l	Algae, 72H, EC50, mg/l
Ba/Ca/Zn carboxylates	not relevant		
Ba/Zn carboxylates	not relevant		
Ba stearate	not relevant		
$CaCl_2$	3130		
Ca/Zn carboxylates	not relevant		
K/Zn carboxylates	not relevant		
Mg/Zn carboxylates	not relevant		
Zn carboxylates		52	
Stearic acid, sodium salt	125		
Butyltin carboxylates	not available		
Butyltin mercaptides	0.13–43	0.035-0.38	0.56–1.3
Butyltin mercaptides/carboxylates	not available		
Methyltins	not available		
Methyltin mercaptides	>1000	32	260 96H
Octyltin carboxylates	not available		
Octyltin mercaptides	not available		
Organotin mercaptides	0.6(phenol)–>1000	0.38–32	260 96H
Tributyltin	not available		
Tetrabutyltins	41.6–49.2		

Table 12.12. Toxicity of stabilizers and its products of reaction with HCl to test organisms.

Stabilizer group	Fish, 96H, LC50, mg/kg	Daphnia magna, 48H, EC50, mg/l	Algae, 72H, EC50, mg/l
Lead oxide	not available		
Lead stearate	not available		
Lead sulfate	not available		
Dibasic lead phosphite	not available		
Dibasic lead phthalate	not available		
Dibasic lead stearate	not available		
Dibasic lead sulfate	not available		
Tribasic lead maleate	not available		
Tribasic lead sulfate	not available		
Tetrabasic lead fumarate	not available		
Tetrabasic lead sulfate	not available		
Benzophenones	>100	16-52	56–>100
Benzotriazoles	>67–>100	15–>100	>10–>100
Cyanoacrylates	not available		
HALS	>100->2500	20-25	>100
Oxalanilides	>100	643	
Phenolic antioxidants	43–>100	55–>1000	>30–>1000
Phosphites	66–>100	0.42–510	>75.2–>100

Two conclusions are pertinent from Table 12.12:

- there are many gaps in the available data. The term "not relevant" was coined by some manufacturers to mean that because of very low water solubility, the chemical was thought to not be toxic and therefore testing was not done. Also, there is a surprising number of "not available" comments to signal that many stabilizers produced for more than half of a century have not been tested.
- with the exception of some tin compounds, the toxicity of stabilizers is generally low.

Bioactivities of organotins including anti-cancer, antiviral, antiparasitic, antimicrobial, antihypertensive activities and anti-hyperbilirubinemia are known and their anti-cancer abilities are extensively studied.[61] Their high toxicity have limited their application as drugs, despite their multiple biological activities.[61] Reproductive toxicity, neurotoxicity and other toxic effects can be caused by these compounds.[61] Trimethyltin chloride (TMT) is a neurotoxicant to embryonic zebrafish.[62]

Toxicity and environmental impact of plasticizers,[63,64] antistatics,[65,66] and antiblocking, release, and slip additives[67,68] have been thoroughly discussed in separate monographs and databases referenced below.

12.9 LIFECYCLE ASSESSMENT

Life cycle assessment of recycling PVC window frames has been made.[69] Replacing virgin polymer by PVC from post-consumer waste saves around 2 t of CO_2 eq./t of PVC while PVC from post-industrial waste saves 1.8 t.[69] Metal recycling influences the environmental savings (virgin aluminium saves 54 times more CO_2 eq./t than recycled PVC).[69] Recycling of 100 kt/yr of window frames in Europe has a potential to save around 200 kt of CO_2 eq./yr.[69] Recycling of PVC windows is currently in its infancy.[69]

An incineration process and a vacuum pyrolysis process for energy conversion were compared as potential utilization of PVC waste.[70] Electrical power output per unit mass of PVC waste in the incineration process was twice as high as that of the vacuum pyrolysis process. Incineration of PVC produced 300 ng/100 kg of dioxins and vacuum pyrolysis 98.19 ng/100 kg of dioxins.[70]

12.10 REFORMULATION IN WASTE PROCESSING

Development of formulation for extruded foam PVC building products aimed at sustainable green technology, which is based on cost-effective formulation suitable for recycling.[71] A balanced stabilizer and lubricant formulation helps to overcome the effects of repeated heat history on the recycled/regrind PVC.[71] A formulation containing 70% of recycled PVC was implemented.[71]

12.11 PHOTODEGRADABLE PVC

Nanocomposite film was prepared by embedding a nano-TiO_2 photocatalyst modified by bismuth oxyiodide into the commercial PVC plastic.[72] The film had higher photocatalytic degradation activity than film without bismuth catalyst.[72] Weight loss of the film was 30.8% after 336 h of exposure (1.5 times higher than film without catalyst).[72] In still another version polyoxymetalate catalyst was added.[73] Similar weight loss was obtained.[73]

UV radiation and treatment with H_2O_2 were used to degrade PVC containing bis-2-ethylhexyl phthalate.[74] The addition of plasticizer to PVC protected the surface and bulk from damage by UV/H_2O_2.[74] Without plasticizer, the polymer was susceptible to radical attack by OH radicals.[74]

12.12 ENERGY RECOVERY

In the first step, chlorine removal by a pyrolysis process is used prior to a subsequent thermal treatment for energetic valorization.[75] HCl is removed at low temperature (340^{o}C) before the carbonaceous residue is subjected to a subsequent thermal treatment for energetic valorization. Hydrochloric acid and syngas are obtained as a result.[75]

The removal of HCl was also considered in Japan, where chlorine content must be below 100 ppm.[76] A single-screw extruder was used for the dechlorination process of municipal wastes because it also has a short residence time.[76]

12.13 WASTE PROCESSING

Oily products are formed from PVC after 3 h of reaction time at 200°C.[77] The enhanced dehydrochlorination is accompanied with rapid chain scission without any detectable crosslinking.[77] Thermal zip elimination of HCl occurs and oxidation leads to scission of polyenes producing low molecular weight fragments.[77] The chain breaking takes place mostly in the middle of the conjugated polyene.[77] An overview of water treatment technology can be found elsewhere.[78]

Acid-catalyzed conversion of chlorinated plastic waste into valuable hydrocarbons has been studied.[79] A mixture of postconsumer plastic waste (HDPE/LDPE/PP/PVC) was pyrolyzed over cracking catalysts using a fluidizing reaction system.[79] A kinetic and mechanistic model was used to predict production rates and product selectivity for the catalytic degradation of polymers.[79]

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